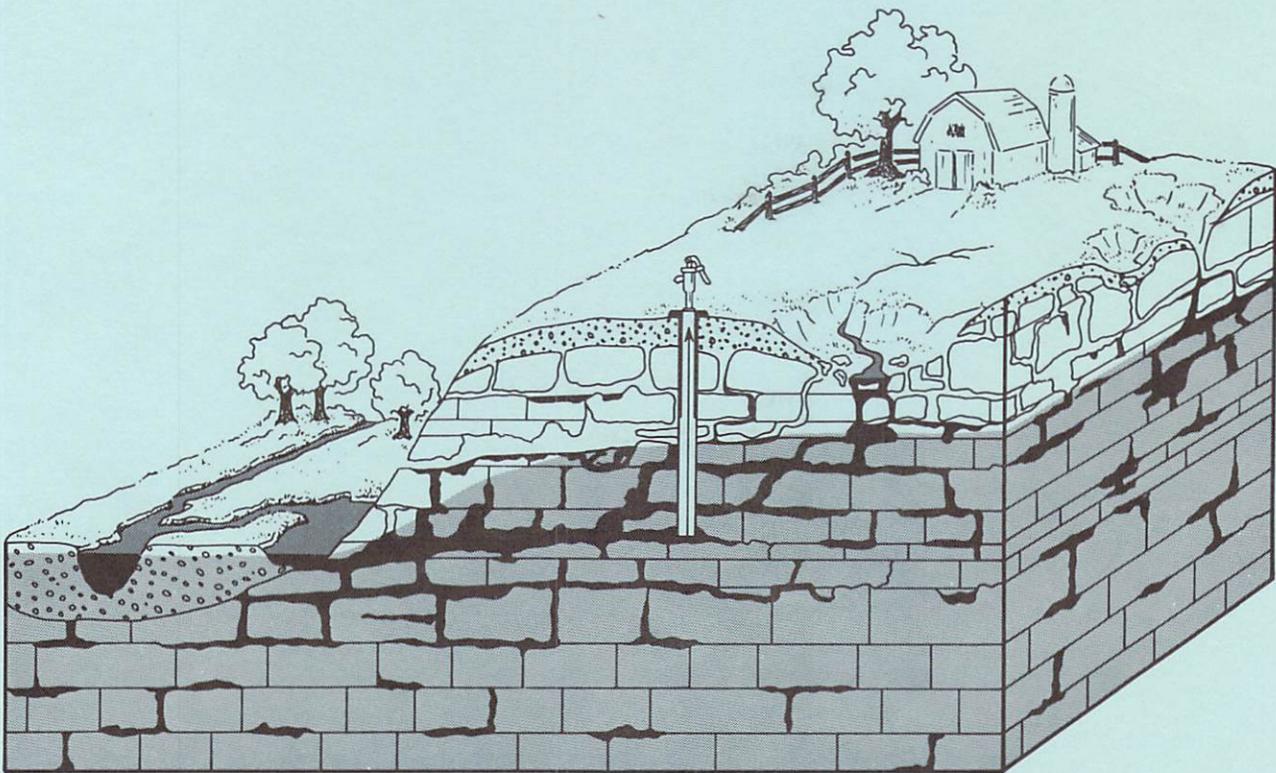


HYDROGEOLOGIC AND WATER QUALITY INVESTIGATIONS IN THE BIG SPRING BASIN, CLAYTON COUNTY, IOWA

1983 WATER – YEAR

George R. Hallberg • Robert D. Libra • E. Arthur Bettis III • Bernard E. Hoyer



Iowa Geological Survey

Donald L. Koch, State Geologist and Director

123 North Capitol Street

Iowa City, Iowa 52242

The publication of this document has been financially aided through a grant from the United States Environmental Protection Agency and a cooperative agreement with the U.S. Department of Agriculture, Soil Conservation Service.

HYDROGEOLOGIC AND WATER QUALITY INVESTIGATIONS IN THE
BIG SPRING BASIN, CLAYTON COUNTY, IOWA; 1983 WATER-YEAR

George R. Hallberg
Chief, Geological Studies Division

Robert D. Libra
Hydrogeologist, Geological Studies Division

E. Arthur Bettis III
Research Geologist, Technical Services Division

Bernard E. Hoyer
Chief, Technical Services Division

Iowa Geological Survey
Donald L. Koch, State Geologist and Director
123 North Capitol Street
Iowa City, Iowa 52242

The publication of this document has
been financially aided through a grant
from the United States Environmental Protection Agency
and a cooperative agreement with the U.S. Department
of Agriculture, Soil Conservation Service

FOREWORD

This is the fifth report describing on-going investigations of groundwater quality in northeastern Iowa, and the third report dealing with results from work in the Big Spring basin in particular. The Big Spring area, because of its unique setting, affords many insights into the behavior of the hydrogeologic system of northeastern Iowa, and interactions between surficially applied chemicals and shallow groundwater quality that pertain to all of Iowa, as well as much of the Corn Belt. Many agencies and individuals are involved with this work, and they are noted in the acknowledgements. Work continues in the Big Spring basin area as state, federal, and local agencies strive to gain the experience and data necessary to effect a satisfactory balance between efficient agricultural production and protection of water supplies.

Donald L. Koch
Director and State Geologist

IN MEMORIAM

TAUN NOVAK

The authors and all at the Iowa Geological Survey who knew her, recognize the contributions Taun Novak made to recent groundwater studies in Northeast Iowa. As the Iowa coordinator for the U.S. Environmental Protection Agency, Underground Injection Control Program, Taun provided constant support for our environmental assessment. She was an able coordinator; she became a friend. Her accidental death remains a sorrowful memory. We hope that continuing groundwater protection programs and improved water quality may be her memorial.

HYDROGEOLOGIC AND WATER QUALITY INVESTIGATIONS IN THE
BIG SPRING BASIN, CLAYTON COUNTY, IOWA; 1983 WATER-YEAR

George R. Hallberg
Robert D. Libra
E. Arthur Bettis III
Bernard E. Hoyer

Iowa Geological Survey

ABSTRACT

Water-year 1983, the second complete year of monitoring in the Big Spring basin, provides some interesting contrasts to the first year of study in the region. Significantly more detailed hydrologic and water-chemical monitoring were done for particular hydrologic events.

There was a dramatic change in land management in the basin because of the PIK program. Reduction in total corn acreage and slight reductions in fertilization rates produced about a 30-40% decrease in N-fertilizer application for the basin, and a somewhat lesser decrease in pesticide use.

Precipitation in WY-1983 totalled 44.5 inches (1,130mm); an increase of 31% from WY-1982. The total range of (instantaneous) discharges measured at Big Spring, from 32 to 295 cfs (0.9 - 8.4 cms) was nearly identical for the two years. However, the greater precipitation increased the total water discharged from the basin by about 47% over WY-1982; surfacewater discharge increased 100% and groundwater discharge (disregarding WY-1982 storage changes) increased 37%. The total water-yield equalled about 49% of precipitation. For groundwater, the runin, conduit-flow component increased 34% while the infiltration, base-flow component increased 8% (WY-1982 storage effects cannot be removed from this figure). Even with the greater discharge these groundwater components still occur in the same relative balance over the course of a water-year, with the runin, conduit-flow component comprising only 11% of the groundwater discharge, while the infiltration component comprised 89% of the discharge.

The greater water discharge, and particularly the greater groundwater movement through the soil in infiltration caused a significant increase in chemical discharge from the basin. Total nitrate-N discharged from the basin in WY-1983 increased 58% from WY-1982, and totalled more than 1,430 tons (13×10^5 kg) of N; approximately 755 tons (6.9×10^5 kg) in groundwater, and 675 tons (6.1×10^5 kg) in stream-flow. This equals about 43 lbs-N/ac (49 kg-N/ha) for the entire basin. The flow-weighted mean nitrate concentration in groundwater increased from 39 mg/l in WY-1982 to 46 mg/l in WY-1983. Thus, the mean ni-

trate concentration for the basin exceeded the the 45 mg/l drinking water standard.

Similar trends were recorded on the regional basis as well. The discharge of the Turkey River at Garber increased 40% from WY-1982, and the total $\text{NO}_3\text{-N}$ discharged from the Turkey River basin was approximately 13,400 tons-N ($12.1 \times 10^6 \text{kg-N}$) (up from 9,400 tons of N in WY-1982). This is an equivalent of 27 lbs-N/ac (30 kg-N/ha) for the entire region.

The discharge of the herbicide atrazine in groundwater increased 120% over WY-1982. However, this still only amounted to about 31 lbs (14 kg) of atrazine. Atrazine was the only pesticide detected in groundwater year-round, with concentrations ranging from 0.1 to 5.1 $\mu\text{g/l}$, with a flow-weighted mean of 0.28 $\mu\text{g/l}$. Four other commonly used herbicides were intermittently detected in groundwater, but primarily during runin-recharge events in May, June, and July. These herbicides were (maximum concentrations noted in parantheses, before common name): Lasso (0.63 $\mu\text{g/l}$, alachlor); Bladex (1.2 $\mu\text{g/l}$, cyanazine); and Dual (0.62 $\mu\text{g/l}$, metolachlor). Lasso appeared in groundwater as late as 8/30/83. The insecticide Dyfonate (fonofos) also appeared in groundwater (0.11 $\mu\text{g/l}$) during a large runin-recharge, storm event. Even though the amount and concentration of pesticides in water increased substantially in WY-1983, the total mass discharged is still estimated at only about 5% of that normally applied. Numerous other pesticides that were applied in the basin were not detected in groundwater.

Large spring or early summer runoff and discharge events can significantly affect the total pesticides lost in water. During the two week period of large runoff-discharge events in late-June and early-July about 35% of the total discharge of atrazine occurred. The amount discharged during this period alone equaled about 80% of the atrazine discharged in WY-1982.

The contributions of the components of the groundwater discharge were approximately the same in WY-1983 as in WY-1982; the infiltration, base-flow component comprising about 90% of the water discharge, and the runin, conduit-flow component only 10%. The highest concentrations and largest mass of nitrate are delivered through the infiltration-component (95%) while the runin-component delivered only 5% of the nitrate-N; similar to WY-1982. With the large runoff-runin events, the relative delivery of pesticides (based on atrazine) to groundwater was substantially different. In WY-1983 the runin component delivered 47% of the pesticides, with a flow-weighted mean atrazine concentration of 1.2 $\mu\text{g/l}$, while the infiltration component delivered 53% of the pesticides, with a flow-weighted mean atrazine concentration of only 0.16 $\mu\text{g/l}$. Even with the different conditions of WY-1983 the infiltration component still delivers the largest mass of contaminants into the groundwater system. The respective contributions of these components must be considered in any planning of remedial measures or management practices.

Nitrate concentrations monitored from tile-lines, surfacewater sites, Big Spring and the Turkey River all fluctuate in harmony throughout the years of monitoring. The parallel nature of the records demonstrate that similar mechanisms and responses to recharge deliver nitrate to all parts of the hydrologic system. The close coincidence of both nitrate and discharge records between Big Spring and the Turkey River show that the processes and relationships documented at Big Spring are applicable on the regional scale as well.

The total $\text{NO}_3\text{-N}$ losses from the Big Spring basin increased from an equivalent of 27 lbs-N/ac (31 kg-N/ha) in WY-1982 to 43 lbs-N/ac (49 kg-N/ha) in WY-1983. Obviously, there is no direct relationship between the $\text{NO}_3\text{-N}$ discharged and the decreased application of fertilizer-N which resulted from the PIK program in calendar year 1983. This is because of the time lag between changes in chemical land-treatment and changes in the chemical quality of the groundwater (combined with differences between crop, or calendar years and water-years). As shown by a review of various agronomic studies, at moderate to high N-fertilization rates $\text{NO}_3\text{-N}$ is stored in the soil, and the amount builds up in direct proportion to the amounts applied and the number of years of application. The $\text{NO}_3\text{-N}$ leached in any year, such as WY-1983, is in large part, related to this storage, which masks the effects of individual years in the short term. Any impact, or decrease in $\text{NO}_3\text{-N}$ leaching resulting from PIK, would be expected to show in future monitoring. Landuse in the Big Spring basin has been relatively constant between 1979 and 1983, and thus the $\text{NO}_3\text{-N}$ losses can be put in the context of the acreage that has been in corn production over that time (3-5 years in various rotations). In this perspective the amount of N lost from this acreage base increased from 47 lbs-N/ac (52 kg-N/ha) in WY-1982 to 74 lbs-N/ac (83 kg-N/ha) in WY 1983. The WY-1982 N-losses were equivalent to 33% of the fertilizer-N applied in 1982; the WY-1983 N-losses would be equivalent to 53% of those same 1982 N-fertilizer amounts. Note that this is a minimum figure because it only accounts for $\text{NO}_3\text{-N}$ losses. Thus, in a relatively wet year, such as WY-1983, a minimum equivalent to about 50% of the chemical fertilizer-N applied may be lost into groundwater and surfacewater combined. Particularly considering how well the behavior in the Big Spring system reflects regional conditions, the magnitude of N-losses would certainly seem to constitute an economic as well as an environmental loss.

As noted these figures are minimums for the amount of N lost from the basin. Piezometer studies and stream monitoring in the basin show that denitrification occurs in local-settings in the soil environment, and possibly in the streams themselves, accounting for additional lost N, that cannot be quantified. Monitoring of ammonium-N and organic-N show that these forms of N are also discharged in groundwater during runoff-recharge events. They are discharged in higher quantities in streamflow which leaves the basin. In total they may constitute 10% additional to the N lost from the basin. In the alluvial aquifers where denitrification removed the NO_3 , pesticides were still present in the groundwater.

In the unique karst-carbonate aquifer system suspended-sediment also occurs in groundwater causing water-quality problems, particularly during runoff, conduit flow periods. During peak, conduit-flow the sediment loads are essentially equal to surface-runoff water, reaching concentrations of nearly 5,000 mg/l and discharge rates of over 190,000 lbs/hr (87,000 kg/hr). The total discharge of suspended sediment at Big Spring alone was about 3,500 tons (3.2×10^6 kg). These sediment loads create serious problems for the ICC fish hatchery operations.

Detailed monitoring of discharge and water chemistry, dye tracing, and hydrograph analysis of major discharge events during WY-1983 provide many insights to the behavior of the karst-hydrogeologic system. These data verify, and amplify, the prior findings about the flow system and the nature of the contributing components. While the recharge-discharge mechanisms are complex,

different analytical and chemical hydrograph separation techniques show that the two fundamental components--infiltration base-flow, and runoff conduit-flow--can be consistently quantified within about 10%. The chemical monitoring and separation techniques also verify the complexity of components which contribute to major discharge-hydrograph events, and contribute to the nature of water-quality fluctuations.

Monitoring of rainfall-runoff events shows that the high surfacewater concentrations of parameters such as suspended sediment (e.g., 5,000 mg/l), pesticides (5-20 $\mu\text{g/l}$), organic and ammonium-N move through the conduit-groundwater system as a 'slug' discharging from the groundwater in essentially the same concentration as they entered. These events also introduce bacteria and potentially pathogenic organisms into groundwater. While the runoff component delivers contaminants to the groundwater which are of concern for public health on the local level, the infiltration component is responsible for regional aquifer contamination. Also, infiltration is the recharge mechanism common to all aquifers, which gives these data much broader implications.

Numerous soil cores were collected from the basin, to varying depths, under various landuse, after corn-harvest in 1982 and 1983. The soil samples were analyzed for $\text{NO}_3\text{-N}$ and pesticides. The amount of $\text{NO}_3\text{-N}$ stored in the profile vary directly with landuse and increased proportionately with the number of years of fertilized corn. Measured to a depth of 10 feet (3 m) the amount of $\text{NO}_3\text{-N}$ stored in soils under forest, pasture, fertilized-pasture and alfalfa-meadow (in rotation with corn) ranged from 48-80 lbs-N/ac (50-90 kg-N/ac) while under high fertilization corn the amounts ranged from 135 lbs-N/ha (150kg-N/ha) under second-year corn to 400 lbs-N/ac (450 kg-N/ha) under 'continuous' corn.

In the plow-layer maximum concentrations of 120.0 $\mu\text{g/kg}$ atrazine, 5.8 $\mu\text{g/kg}$ Bladex (cyanazine), 23.0 $\mu\text{g/kg}$ Lasso (alachlor) and 10.0 $\mu\text{g/kg}$ Dyfonate (fonofos) were recorded. Atrazine concentrations of 1.0 $\mu\text{g/kg}$ were noted to depths of nearly 10 feet (3.0 m), and 0.3 $\mu\text{g/kg}$ atrazine were detected at a depth of 14.5 feet (4.4 m) at one location. Other pesticides were not detected at great depths.

Other water-quality and crop-use data collected in the region further support the direct, linear relationship, between the increase in nitrates in groundwater with the large increase in N-fertilization that has taken place since the 1960s. A review of agronomic studies which have related N-fertilizer application rates to the N-buildup in soils or the N-losses in tile drainage, show that this linear relationship is the response that should be predicted in a setting such as northeastern Iowa. The direct relationships between total fertilizer-N applications and groundwater nitrate concentrations also indicate that any significant decrease in the amounts of fertilizer-N applied (or increased efficiency of N-use, such that less could be leached) would be accompanied by a proportional decrease in groundwater nitrate, at least when integrated over a 2-5 year period.

On the short term, seasonal or monthly basis, the concentration of NO_3 and mass of $\text{NO}_3\text{-N}$ discharged show significant, positive, linear relations to the amount of water discharged. Over the long term the excess $\text{NO}_3\text{-N}$ is stored in the soil. Because infiltration through the soil is the principle component of

recharge, the timing of nitrate fluctuations in water supplies is related to seasonal recharge periods, and generally not to the timing of seasonal agricultural practices.

Management alternatives, or 'best-management practices' (BMPs), need to be formulated that will couple standard concerns for soil erosion and surface-water quality with the need to reduce chemical losses in infiltration to groundwater. This will need to be done to balance our need for efficient agricultural production with the need for safe drinking water. Some measures will control soil erosion and runoff but will promote greater infiltration and additional chemical leaching. Over time these problems can be addressed through new technology. However, a review of many studies suggests that through new combinations of many current and accepted practices these goals can be compatible. Better chemical and nutrient management must be coupled with systems for soil management, as well.

TABLE OF CONTENTS

	<u>Page No.</u>
FORWORD	ii
In Memoriam	ii
ABSTRACT	iii
TABLE OF CONTENTS	viii
LIST OF FIGURES	xi
LIST OF TABLES	xiv
LIST OF APPENDICES	xvi
ACKNOWLEDGEMENTS	xvii
INTRODUCTION	1
1983 Landuse and Management	2
HYDROLOGIC MONITORING	2
Climate and Discharge	3
<u>Climatic Data</u>	3
<u>Groundwater Discharge</u>	5
<u>Total Groundwater Basin and Turkey River Discharges</u>	7
Water Balance	11
<u>Groundwater Balance</u>	11
<u>Surfacewater Discharge</u>	14
<u>Water-Balance Summary</u>	14
WATER QUALITY MONITORING	15
Nitrate Data From Big Spring	15
Nitrate Data From the Monitoring Network	19
Nitrate-N Discharge	20
<u>Regional Nitrate-N Discharge from the Turkey River</u>	21
Pesticide Monitoring - Big Spring	26
<u>Atrazine Discharge</u>	30
Hydrograph Separations: Runin and Infiltration Components of Groundwater Discharge	30
Comparison of 1982 and 1983 Water-Years	31
<u>NO₃-N Losses and Landuse</u>	35
MONITORING OF MAJOR DISCHARGE EVENTS	37

TABLE OF CONTENTS (continued)

	<u>Page No.</u>
Snowmelt Period Discharge Events -- 2/14/83-2/27/83.	37
<u>Hydrograph Separation</u>	42
April 1983, Discharge Events.	47
Summer Discharge Event.	50
<u>Antecedant Conditions and Precipitation</u>	51
<u>Surfacewater Discharge and Water Quality</u>	52
<u>Dye-Traces</u>	56
Dye Trace Method.	56
Discussion of Dye Trace Results	57
Interpretation of the Dye-Trace Results	59
<u>Groundwater Discharge</u>	62
<u>Groundwater Quality</u>	63
Run-in, Conduit Flow Components:	64
1. Suspended Sediment.	64
2. Organic-N, Ammonium-N	66
3. Pesticides.	67
4. Other Water-Quality Parameters.	70
Infiltration Component.	71
1. Nitrates.	71
Discussion of the Nitrate Data.	74
2. Other Infiltration Parameters	81
<u>Hydrograph Separation</u>	81
Chemical Delivery by Flow Components.	83
Tile-Line Monitoring: A Proxy of Shallow Groundwater Quality Responses	85
SUSPENDED SEDIMENT, ORGANIC-N, AND AMMONIUM-N: PROPERTIES AND ESTIMATES OF ANNUAL DISCHARGE	92
Suspended Sediment.	92
Organic-N, Ammonium-N	93
NITRATE AND PESTICIDE ANALYSES FROM SOIL CORES	93

TABLE OF CONTENTS (continued)

	<u>Page No.</u>
Soil Nitrates	95
Soil Pesticides	105
NITRATE AND PESTICIDE ANALYSES FROM IGS PIEZOMETERS.	106
Denitrification In An Alluvial Aquifer.	107
LANDUSE AND WATER-QUALITY CHANGES OVER TIME IN THE BIG SPRING BASIN.	111
AGRONOMIC STUDIES OF N-FERTILIZATION AND LEACHING OF NITRATE BELOW THE ROOT ZONE.	112
WATER QUALITY AND AGRICULTURAL MANAGEMENT.	120
Further Notes on Management Practices	124
Reduced Tillage Effects on Nitrogen Losses.	130
SUMMARY AND DISCUSSION	133
Overview WY-1983.	133
Components of Groundwater and Chemical Discharge.	134
Nitrate Fluctuations and the Hydrogeologic System	135
NO ₃ -N Losses and Landuse	135
Suspended Sediment in Groundwater	136
Detailed Monitoring of Discharge Events	136
Soil Nitrates	138
Soil Pesticides	138
Temporal Changes in Water-Quality	140
Review of Agricultural Management Practices and Water-Quality	141
REFERENCES CITED	142
APPENDIX-1, Standard Water-Quality Data From All Monitoring Sites.	154
APPENDIX-2, Water Mineral-Scan Analyses From Various Monitoring Sites.	214
APPENDIX-3, Chemical Analyses From Soil Profile Samples From The Big Spring Basin.	221

(CONTINUED)
LIST OF FIGURES

<u>Number</u>	<u>Title</u>	<u>Page No.</u>
1.	Discharge hydrograph from Big Spring; 24-hour precipitation, maximum and minimum daily temperatures, temperature and specific conductance of groundwater discharging at Big Spring, for Water-Year 1983.	8
2.	Discharge hydrographs from the Turkey River at Garber and the Big Spring groundwater basin; nitrate concentrations from the Big Spring and Turkey River; and atrazine concentration from Big Spring, for water-year 1983.	12
3.	Water quality sample sites in Big Spring study area	16
4.	Topographic map of Bugenhagen basin, showing sampling sites	17
5.	Topographic map of Sass basin, showing sampling sites	18
6.	Nitrate concentrations over time for Big Spring, tile-line drainage water (sites 108, L22-T, and BTL-UW) and Silver Creek (site 109, L23-S.).	21
7.	Nitrate concentrations over time for Big Spring and two monitoring stations on Roberts Creek (sites 110, F-45; 111, F-47).	22
8.	Nitrate concentrations for Big Spring and the Turkey River.	22
9.	Comparison of nitrate concentrations at Big Spring for 1983 (black) and 1982 (gray) water-year	35
10.	Total monthly water discharge at Big Spring vs. monthly flow-weighted, mean nitrate concentration at Big Spring	37
11.	Total monthly water discharge at Big Spring, vs. total monthly nitrate discharge at Big Spring.	38
12.	Groundwater discharge and nitrate concentration at Big Spring during February, 1983, snowmelt event.	41
13.	Analytical hydrograph separation of February, 1983, snowmelt event.	44
14.	Nitrate (chemical)-based hydrograph separation for February, 1983, snowmelt event	45
15.	"Offset" nitrate (chemical)-based hydrograph separation for February, 1983, snowmelt event	46
16.	Groundwater discharge and nitrate concentrations at Big Spring during spring, 1983, events.	49

LIST OF FIGURES (Continued)

<u>Number</u>	<u>Title</u>	<u>Page No.</u>
17.	Groundwater discharge and precipitation data for Big Spring during mid-summer discharge event.	52
18.	Surfacewater discharge and water-quality at Boog D, which drains into sinkholes.	54
19.	Nitrate concentrations in tile drainage water and surface water during mid-summer event.	55
20.	Locations of sinkholes and major sinkhole surface-drainage basins; location of sinkholes used for dye-input during dye traces; and idealized (straight-line) dye flow path to Big Spring	58
21.	Fluorescent-dye concentration in groundwater at Big Spring from 'double' dye trace during mid-summer event; groundwater discharge record shown in gray for comparison	60
22.	Specific conductance of the groundwater at Big Spring during mid-summer event; groundwater discharge shown as gray background for comparison.	65
23.	Suspended-sediment concentration in groundwater at Big Spring during mid-summer event.	66
24.	Mass of suspended-sediment discharged with groundwater at Big Spring during mid-summer event	67
25.	Concentration of organic-N and ammonium-N in groundwater at Big Spring during mid-summer event.	69
26.	Log-log plot of organic-N vs. suspended sediment concentration in groundwater from Big Spring	70
27.	Total pesticide and atrazine concentration in groundwater at Big Spring during mid-summer event	71
28.	Total pesticide vs. suspended sediment concentration in groundwater from Big Spring, during mid-summer event	72
29.	Mass of atrazine and NO ₃ -N discharged with groundwater at Big Spring during mid-summer event	72
30.	Total iron vs. suspended sediment concentration in groundwater at Big Spring, during mid-summer event.	74
31.	Nitrate concentration in groundwater at Big Spring, during mid-summer event	75
32.	Analytical hydrograph separation of the mid-summer event. . . .	82

LIST OF FIGURES (Continued)

<u>Number</u>	<u>Title</u>	<u>Page No.</u>
33.	Hydrograph separation of the mid-summer event using specific conductance	84
34.	Nitrate concentrations and discharge notes from October event for Big Spring and various tile lines and surfacewater sites .	90
35.	Depth distribution of nitrate stored in soil profile under different landuse.	98
36.	Cumulative kg-NO ₃ -N/ha stored in soil profile under different landuse.	102
37.	Estimated tons of fertilizer-and manure-nitrogen applied in the Big Spring basin, and average nitrate concentration in groundwater at Big Spring, shown in gray (from Hallberg et al., 1983, p. 160). Estimated maximum amount of N harvested with corn shown in black	114
38.	Increase in N-fertilizer use over time in Iowa, Illinois, and France in relation to N-removed in crops and groundwater quality	115
39.	Midwestern experiment farm studies showing relationship between N-fertilization rate (kg-N/ha) and the amount of NO ₃ -N (kg-N/ha) stored in the soil to a given depth after specified time of treatment.	117
40.	Percentage of fertilizer-N recovered in soil and grain (corrected for no-fertilizer-N check plot); Iowa; Moody SiCL; 17 years treatment; from Jolley, 1974	119
41.	Midwestern experiment farm studies showing relationship between N-fertilization rate (kg-N/ha) and the amount (kg-N/ha) of NO ₃ -N lost in tile-drainage, and the flow-weighted average NO ₃ concentration in the tile-drainage water.	121
42.	NO ₃ -N losses in sub-surface seepage water: Iowa; Western Iowa Loess-soils; 5 years treatment; Burwell et al., 1976	123
43.	Relationships among N-fertilization rate, the amount of NO ₃ -N stored in the soil profile, and crop-rotations; Wisconsin; Rosetta SiL; 4 years rotation treatment; Olsen et al., 1970. .	123

LIST OF TABLES

<u>Number</u>	<u>Title</u>	<u>Page No.</u>
1.	Landuse in 1983 in Big Spring basin;.	3
2.	Summary of pesticides known to be used in the Big Spring basin.	4
3.	Climatic data for stations near Big Spring basin, and estimates for Big Spring basin from intermittent monitoring.	6
4.	Monthly summary of groundwater discharge data for the Big Spring basin for water-year 1983	10
5.	Total water yield from Big Spring basin for Water-Year 1983 (10/1/82 - 9/30/83).	15
6.	1983 Water-year summary of groundwater and chemical discharge from Big Spring basin to the Turkey River	23
7.	Monthly summary of nitrate-N output with groundwater discharged from the Big Spring basin to the Turkey River; 1983 water-year.	24
8.	Total water and nitrate yield from Big Spring basin for the 1983 water-year; 10/1/82-9/30/83	25
9.	Results of UHL analyses for pesticides in water and sediments from Big Spring	27
10.	Components of groundwater and chemical discharge for water-year 1983, from Big Spring basin to Turkey River	32
11.	Comparison of total water and chemical discharge from the Big Spring basin for 1982 and 1983 water-years	34
12.	Maximum measured concentrations for various, currently used, pesticides found in groundwater at Big Spring for WY-1982 and -1983	36
13.	Summary of nitrate-N loss from the Big Spring basin in relation to landuse for 1982-1983 water years	39
14.	Summary of Big Spring analytical hydrograph separation data for the 6/30-7/11/83 events.	85
15.	Analyses of suspended sediment samples from Big Spring.	94
16.	Measured nitrate concentrations and calculated nitrate-N stored in soils under various landuse in the Big Spring basin; summarized by depth.	97

LIST OF TABLES

<u>Number</u>	<u>Title</u>	<u>Page No.</u>
17.	Nitrate-N stored in "shallow loess" derived soils over bedrock.	106
18.	Pesticide concentrations in loess soils under "continuous" corn	108
19.	Water-quality analyses from alluvial wells in the Big Spring basin. Data from adjacent surfacewater and tile lines shown for comparison.	109
20.	Landuse change in the Big Spring Basin, 1970-1980.	113

LIST OF APPENDICES

<u>Number</u>	<u>Title</u>	<u>Page No.</u>
1.	Standard Water-Quality Data From All Monitoring Sites	154
2.	Water Mineral-Scan Analyses From Various Monitoring Sites . . .	214
3.	Chemical Analyses From Soil Profile Samples From The Big Spring Basin	221

ACKNOWLEDGEMENTS

This study was possible only because of the hard work and support of many people besides the authors.

Mr. Jerry Spykerman and his staff at the ICC Big Spring Hatchery were instrumental in maintaining the continuous monitoring of the Big Spring. They also made all their facilities available to us. In particular, Jerry Spykerman's personal efforts at the Spring have enabled much of this project to be successful.

Nearly the entire IGS staff have been involved with this project, and were instrumental in its development. Graphic arts were prepared by Pat Lohmann and Kay Irelan, and the manuscript was typed and formatted by Mary Pat Heitman. Deborah Quade and Gale Ressimeyer provided invaluable assistance with sampling and data handling and data synthesis. Other IGS staff who have made significant contributions, above and beyond the "call of duty," include Mike Bounk, Ross Black, Mike Farmer, Jim Giglierano, Pete Kollasch, Greg Ludvigson, Bob Pyle, Pat Ring, Carol Thompson, and Paul Van Dorpe.

The University Hygienic Laboratory has provided excellent support. They provided sampling equipment and all the water-chemical analytical work, as well as timely answers to the many questions which arose during the study. We especially want to acknowledge the help of Roger Splinter, John Kempf, Gene Ronald, Loren Johnson, Armand Lange, Lee Friell, and Ivan Schwabauer.

Partial funding for this work was provided through a cooperative agreement with the USDA Soil Conservation Service. The support from the Iowa SCS staff has far exceeded just financial contributions. We especially want to acknowledge the help received from Roger Koster, Stan Mitchem, Jim Reel, Dave Gibney, Dennis Miller, Russ Knutson, and Roger Link.

This study was also partially funded through a grant from the U.S. Environmental Protection Agency. As with the SCS, beyond the financial support, the keen interest, cooperation, and assistance of Taun Novak was invaluable in this work.

The Iowa Department of Water, Air, and Waste Management has also provided continuing assistance. In particular, Rick Kelley has provided invaluable assistance in many phases of this work, but particularly in the coordination of inter-agency activities. Personnel from the U. S. Geological Survey, Water Resources Division, Iowa City, also provided valuable assistance and advice. Ivan Burmeister and his staff established the gage and rating curve at Big Spring. The study would not have been possible without this help. Oscar Lara provided unpublished information and valuable guidance and insight to our runoff estimates and water budget analysis.

Many other people have discussed or reviewed some aspects of this research. Their ideas, suggestions, and criticisms were all appreciated. These people include Gerry Miller, Alfred Blackmer, Robert Horton, Min Amemiya, Tom Fenton, Dick Handy, Stu Melvin, Mike Thompson, and Regis Voss from Iowa State University, James Gulliford, Dan Lindquist, and Ed Beardsley from the Iowa Department of Soil Conservation. Special recognition is due to Jim Baker, Depart-

ment of Agricultural Engineering, Iowa State University, for his comments and insights, and for all his past research which provides much of the foundation for the study.

Dave Gibney, Clayton County District Conservationist with SCS, Jim Hosch, Clayton County Extension Director, and Frank Phippen, County ASCS Executive Director, provided valuable assistance in developing local publicity and cooperation. Steve Helfer, County Sanitarian, has provided local information. Jim Kaap, Dubuque Area Extension Specialist has also provided help and assistance on many facets of this study.

Paul Waite, State Climatologist, and Don Menken, Conservation Officer and weather observer, have provided timely delivery of climatologic data.

Last, but clearly, not least, we must acknowledge the excellent support, cooperation, and encouragement of rural residents in the study area. The hospitality and cooperation we have received, in access to private land and wells, has truly been outstanding. In particular, we must specially thank the following and their families: Harold Kuntz, Kevin Ihde, Harold Vorwalds, Norbert Walz, Norbert Fritz, Donald Steva, Ron Schrader, Eugene Voss, William Eno, Barb Rodas, Al Landt, Elmer Bries, Harold Peterson, Ken Keehner, Francis Meisner, Harley Radloff, Ron Trudow, Franklin Wacker, and Ed Sass.

Even though this list of acknowledgements is lengthy, many other individuals who have contributed have gone unmentioned. A general word of thanks to all those who have helped.

INTRODUCTION

This report will describe the results from the second full water-year (1983) of hydrogeologic and water-quality investigations in the Big Spring basin. The hydrogeologic framework, historic water quality, present and past land-management and chemical management, lab procedures and analytical methods, as well as 1982 monitoring results and interpretations have been described previously by Hallberg and others (1983, 1984), and will not be reiterated here.

During 1983 the water quality sampling scheme was altered from that of 1982 because of different objectives, what was learned from the prior years' results, and available funding. Less effort was placed on well monitoring while the Big Spring and various surfacewater and tile line sites were monitored much more intensively. This was done to further isolate the details of how the hydrogeologic system of the Big Spring basin responds to hydrologic events. For example, Big Spring was sampled at least weekly for analyses of nitrate and pesticide concentrations. During particular 'runoff events' samples were often collected every one or two hours. For water-year 1983, 248 nitrate samples and 81 pesticide samples were analyzed from Big Spring. In addition a number of samples were analyzed for nitrogen-series (NO_3 , NO_2 , ammonium-N, and organic-N), total mineral analyses, and suspended sediment. Additional dye-tracing was also done.

This report will summarize observations on a standard water-year basis: water-year 1983 ran from 1 October, 1982, through 30 September, 1983. This is in contrast to the 1982 water-year summary (Hallberg et al., 1983) which had to run from 1 November, 1981, through 31 October, 1982, because of when sampling began on the project. This one month difference (and overlap) in reporting makes no significant difference in the water-year summaries because October was a low-flow period and had little impact on the total volume of water and chemicals discharged.

By convention (from past reports) the concentration of nitrate will be used in this report as mg/l of NO_3 , unless otherwise stated. NO_3 can be converted, approximately, to mg/l of $\text{NO}_3\text{-N}$ by dividing the NO_3 value by 4.5. When the mass of nitrogen discharged from a site is calculated it is converted from NO_3 to N ($\text{NO}_3\text{-N}$). Concentrations of other forms of nitrogen compounds (ammonium-N, organic-N) are reported as N.

The report will be divided into four components. First, the basic events and record of the water-year will be summarized. Second, the details of monitoring of particular discharge events, and the insights they provided, will be described. Third, a variety of other observations (e.g., from soil cores, etc.) will be outlined. The last component will integrate and summarize the findings and interpretations from all the research to date.

1983 Landuse and Management

Landuse and land management changed dramatically in 1983 because of the U.S.D.A. Payment-In-Kind (PIK) program. Clayton County and the Big Spring basin had maximum enrollments in PIK. Table 1 shows general figures for 1983 landuse. Of most significance is that the acreage of land in corn production was decreased by 35-40% over the prior three years. This resulted in a dramatic decrease in the amount of fertilizer applied in the basin.

Surveys of chemical use were again (see Hallberg et al., 1983) conducted by SCS and IGS staff. These results suggest that chemical N-fertilizer applications were reduced slightly on the remaining corn acreage, on the average, from 175 lbs-N/ac (195 kg-N/ha) in 1982 to about 150 lbs-N/ac (170 kg-N/ha) in 1983. Pesticide use also decreased because of the PIK acres removed from corn production. The decrease in total pesticide use would not be as direct as with fertilizers because herbicides were applied to some PIK acres to control weeds. In general, on the remaining corn acres the pesticides used and rates of application were the same in 1983 as in 1982. The three most widely used herbicides on corn acres were atrazine, Bladex, and Lasso (Bladex usage was up and Lasso down relatively). Again other herbicides were also used in lesser amounts including Dual, Sutan, Ramrod, and Prowl and minor applications of Eradicane, Roundup, Banvel, and 2, 4-D. The most common insecticides used for corn were Counter and Dyfonate followed by Thimet, Lorsban, Furadan, Amaze, and Savit.

A variety of herbicides were also used for weed and brush control in pastures, hay, oats, fence rows, and on PIK acres. These included Bladex, 2, 4-D, Roundup, Banvel, Eptam, 2,4,5-T, MCPA, Princep, Tordon, and paraquat. Two insecticides were reported as used for insect control on hay: Furadan and Savit. All products are believed to be used at the recommended application rates. Table 2 summarizes the pesticides used in the basin by chemical class and gives the common name for the active chemical ingredients.

HYDROLOGIC MONITORING

Hydrologic monitoring of the Big Spring basin, initiated in November 1981, continued through water-years 1982 and 1983. Monitored parameters include climatological data, groundwater discharge, Turkey River discharge, and various aspects of surfacewater-and groundwater-quality. This section will present and discuss the general results of the monitoring data for the 1983 water-year. Individual runoff events, which were monitored in greater detail, will be discussed in a later section. Certain aspects of the hydrologic system continue to be monitored in 1984. Details of the monitoring system are discussed by Hallberg and others (1983).

Table 1. Landuse in 1983 in Big Spring basin; given in square miles (and percentages).

	1983 ¹	1980-82 ²
Corn	36.38 (35)	60.42 (58)
Conservation Use (PIK areas)	25.19 (24)	
Oats	4.66 (5)	8.40 (8)
Hay, Rotation Pasture, other Cover Crops	27.06 (26)	24.47 (24)
Other (Urban, forest, etc.)	9.95 (10)	9.95 (10)
	<u>103.24 (100)</u>	<u>103.24 (100)</u>

¹ Based on cropland reports compiled by local ASCS officials and survey data data from Roger Koster, SCS.

² Data from Hallberg et al. (1983).

Climate and Discharge

Before discussing the water-quality aspects of the monitoring, the water balance for the basin will be described. These data include the precipitation inputs and groundwater and surfacewater discharge outputs from the basin. Changes in groundwater storage are also estimated.

Climatic Data

Climatic data for the Big Spring area include daily precipitation amounts and temperature extremes from the Elkader, Waukon, and Fayette weather stations. These stations form a triangle that encloses the Big Spring basin. Monthly and annual precipitation data for the water-year, along with the long-term averages, are presented for these stations in Table 3. Estimates for pre-

Table 2. Summary of pesticides known to be used in the Big Spring basin.

Chemical Class	Trade Name	Common Name Active Ingredient
HERBICIDES.		
Amides	Lasso Dual Ramrod	alachlor metolachlor propachlor
Benzoics	Banvel	dicamba
Bipyridiliums	Paraquat	paraquat
Dinitroanilines	Prowl	pendimethalin
Phenoxy	(many) (many) (many)	MCPA 2,4-D 2,4,5-T
Thiocarbamates	Sutan (+) Eradicane Eptam, EPTC	Butylate (+R25688) EPTC + R25788 EPTC
Triazines	Atrazine, AAtrex Bladex Princep	atrazine cyanazine simazine
Miscellaneous	Roundup Tordon	glyphosate picloram
INSECTICIDES		
Organophosphates	Counter Dyfonate Thimet Amaze Lorsban	terbufos fonofos phorate isofenphos chlorpyrifos
Carbamates	Furadan Savit	carbofuran carbaryl

precipitation at Big Spring are given. These values are based on intermittent monitoring at the spring and in the basin, as well as data from the other stations (particularly Elkader, the closest station to the basin). The estimates for precipitation at Big Spring are used as the input to the basin water balance.

Water-year 1982-83 was characterized by high precipitation in the study area. Precipitation was 27% and 29% above long-term averages at the Elkader and Fayette stations, respectively, and 48% above average at Waukon. Monthly precipitation was fairly evenly distributed across the area throughout most of the water year. Major exceptions occurred during June, July, and August, reflecting the effects of thunderstorms that were more localized in occurrence and intensity. The greater amount of precipitation recorded at Waukon for the water-year, relative to the other stations, occurred largely during these summer months.

Groundwater Discharge

Groundwater discharge from the Big Spring basin to the Turkey River was monitored daily at Big Spring, or more frequently when conditions warranted. The discharge hydrograph from the spring is shown on figure 1, along with daily precipitation and temperature data from Big Spring and Elkader. Total basin discharge is estimated to be about 14% greater than the discharge from Big Spring alone, as discussed by Hallberg and others (1983). Monthly summaries of total, average, maximum, and minimum discharge to the Turkey River from the basin as a whole are given in Table 4. Details of the groundwater-flow system within the Galena aquifer in the basin are discussed by Hallberg and others (1983). Discharge rates and responses at Big Spring reflect the volume and rates of recharge occurring within the contributing groundwater basin. While there is no simple relationship between precipitation, recharge, and discharge that sufficiently describes the responses monitored at Big Spring, certain responses are characteristic of individual seasons. The characteristic periods are blocked out by the vertical lines on figure 1. Fall 1982 was characterized by intense rainstorms, which produced high discharge events. These high discharge events reflect both the volume and intensity of the storms, but also demonstrate the effect of precipitation falling on harvested fields under low evapotranspiration conditions. Prior to these fall rains, discharge was less than 30 cfs (0.85 cms). Following the rains, discharge increased to 250 cfs (7.18 cms) and rarely fell below 50 cfs (1.4 cms). The extremely high discharges were caused by surfacewater runoff discharging into (surfacewater 'runin') sinkholes, followed by rapid water movement through the conduit-flow parts of the aquifer. However, the generally high discharges that persisted through much of the period must be related to significant infiltration seepage and slow-to-moderate groundwater flow through the diffuse-flow part of the aquifer.

A lack of precipitation and/or precipitation falling as snow during January and early February 1983 resulted in little or no recharge, and therefore a winter discharge recession, with flow rates falling to 30-35 cfs (0.85 -1.0 cms). During recession periods, the groundwater discharging from the basin is begin released from storage. The slow decrease in discharge

Table 3. Climatic data for stations near Big Spring basin, and estimates for Big Spring basin from intermittent monitoring

	Elkader in (mm)	Fayette in (mm)	Waukon in (mm)	Mean in (mm)	Big Spring in (mm)
1982					
Oct.	3.29 (83.6)	3.06 (77.7)	2.83 (71.9)	3.06 (77.7)	3.29 (83.6)
Nov.	4.53 (115.1)	4.01 (101.9)	4.07 (103.4)	4.20 (106.7)	4.53 (115.1)
Dec.	3.05 (77.5)	3.99 (101.3)	2.17 (55.1)	3.07 (78.0)	3.05 (77.5)
1983					
Jan.	0.71 (18.0)	0.83 (21.1)	0.62 (15.7)	0.72 (18.3)	0.71 (18.0)
Feb.	1.84 (46.7)	1.80 (45.7)	2.05 (52.1)	1.90 (48.3)	1.84 (46.7)
Mar.	2.67 (67.8)	2.03 (51.6)	1.52 (38.6)	2.07 (52.6)	1.93 (49.0)
Apr.	2.91 (73.9)	3.28 (83.3)	2.15 (54.6)	2.78 (70.6)	2.91 (73.9)
May	6.44 (163.4)	7.40 (188.0)	7.23 (183.6)	7.02 (178.3)	6.24 (158.5)
June	5.80 (147.3)	5.35 (135.9)	8.39 (213.1)	6.51 (165.4)	8.23 (209.0)
July	5.20 (132.1)	3.46 (87.9)	4.12 (104.6)	4.26 (108.2)	5.92 (150.3)
Aug.	0.69 (17.5)	1.20 (30.5)	6.04 (153.4)	2.64 (67.1)	1.48 (37.6)
Sept.	4.92 (125.0)	5.64 (143.3)	4.49 (114.0)	5.02 (127.5)	4.40 (111.8)
12-month summary	42.05 (1068.1)	42.05 (1068.1)	45.68 (1160.0)	43.25 (1098.6)	44.53 (1131.1)
Oct.	4.02 (102.1)	3.96 (100.6)	3.31 (84.1)	3.76 (95.5)	4.02 (102.1)
Nov.	3.76 (95.5)	4.10 (104.1)	3.69 (93.7)	3.85 (97.8)	3.76 (95.5)
Long-term					
Annual Average					
Precip.					
in. (mm)	33.1 (840.7)	32.5 (825.5)	30.7 (779.8)		
Temp. °F	45	46	45		
°C	7.2	7.8	7.2		

across this period is the result of decreasing gradients, as the potentiometric surface within the Galena aquifer declines.

During late February and early March, snowmelt occurred. Discharge at the spring responded sharply, reflecting 'runin'- recharge and conduit-flow. The rapid rises and falls of the hydrograph show the effects of diurnal temperature variations on melting and runoff. Relatively warm daytime temperatures generated melting and runoff, while the cold evening temperatures did not. These effects are noted at the spring 24-36 hours later. The rapid decrease in discharge that occurred during this period indicate that the remaining snow

pack and/or frozen ground was limiting infiltration recharge to the diffuse-flow parts of the aquifer.

The spring months, March through mid-June, are generally periods of major groundwater recharge in the midwest because of relatively high precipitation and low evapotranspiration. During spring 1983, March and early June were relatively dry, and discharge from Big Spring was accordingly low; 35-45 cfs (1.0 -1.3 cms). However, most of April and May were wet, and discharge from the spring stayed above 60 cfs (1.7 cms) (figure 1). No major runoff-conduit flow events occurred during April and May; discharge exceeded 80 cfs (2.3 cms) for a period of only a few days. The elevated, relatively constant flow rates indicate significant infiltration recharge was occurring.

The summer months, from mid-June essentially through the end of the water year, are generally marked by low precipitation and high evapotranspiration, and therefore insignificant runoff or groundwater recharge. A long, pronounced period where stream and spring discharges recess is the general case. Summer 1983 in the Big Spring area was similar to this expected condition, with the exception of late June and early July. During this one week period, an estimated 9 inches (228 mm) of rain fell; over 6 inches (152 mm) fell in a two-day period. A comparison of the hydrograph and precipitation at Elkader (figure 1) shows that although over 5 inches (127 mm) of precipitation fell during the first three days of this period, runoff was not sufficient to cause discharges over 100 cfs (2.8 cms) at Big Spring. A very intense thunderstorm, delivering over 2 inches (50 mm) of rain in approximately 2 hours, and following in the wake of the previous rains, was needed to generate the major runoff-recharge/high-discharge event noted on the hydrograph. This major event will be discussed in greater detail in a subsequent section. Following this major event, discharge at the spring recessed for most of the remainder of the water year. Rains in excess of 1.5 inches (38 mm) fell during this period but caused only minor recharge to occur, reflecting the low soil moisture and high evapotranspiration conditions existing during the late summer growing season. Seasonal trends and responses noted for water-year 1983 are generally consistent with those noted for water-year 1982 by Hallberg and others (1983).

The monthly summaries of total basin discharge, given in Table 4, highlight the major recharge/discharge periods of the year. About 22% of the discharge for the water-year occurred during November and December. Roughly the same volume of water was discharged during the wet spring months of April and May. The major rain events in late June/early July resulted in a proportionately large total discharge in July also. These five months, which comprise about 42% of the year, accounted for 54% of the total annual discharge. The dry, late summer/early fall months of August, September, and October provide a contrast; during this 25% of the year, only 16% of the total discharge occurred.

Total Groundwater Basin and Turkey River Discharges

The hydrograph in figure 1 shows only measured discharge from Big Spring. Total discharge from the groundwater basin to the Turkey River includes groundwater discharging from two other small springs, as discussed by Hallberg

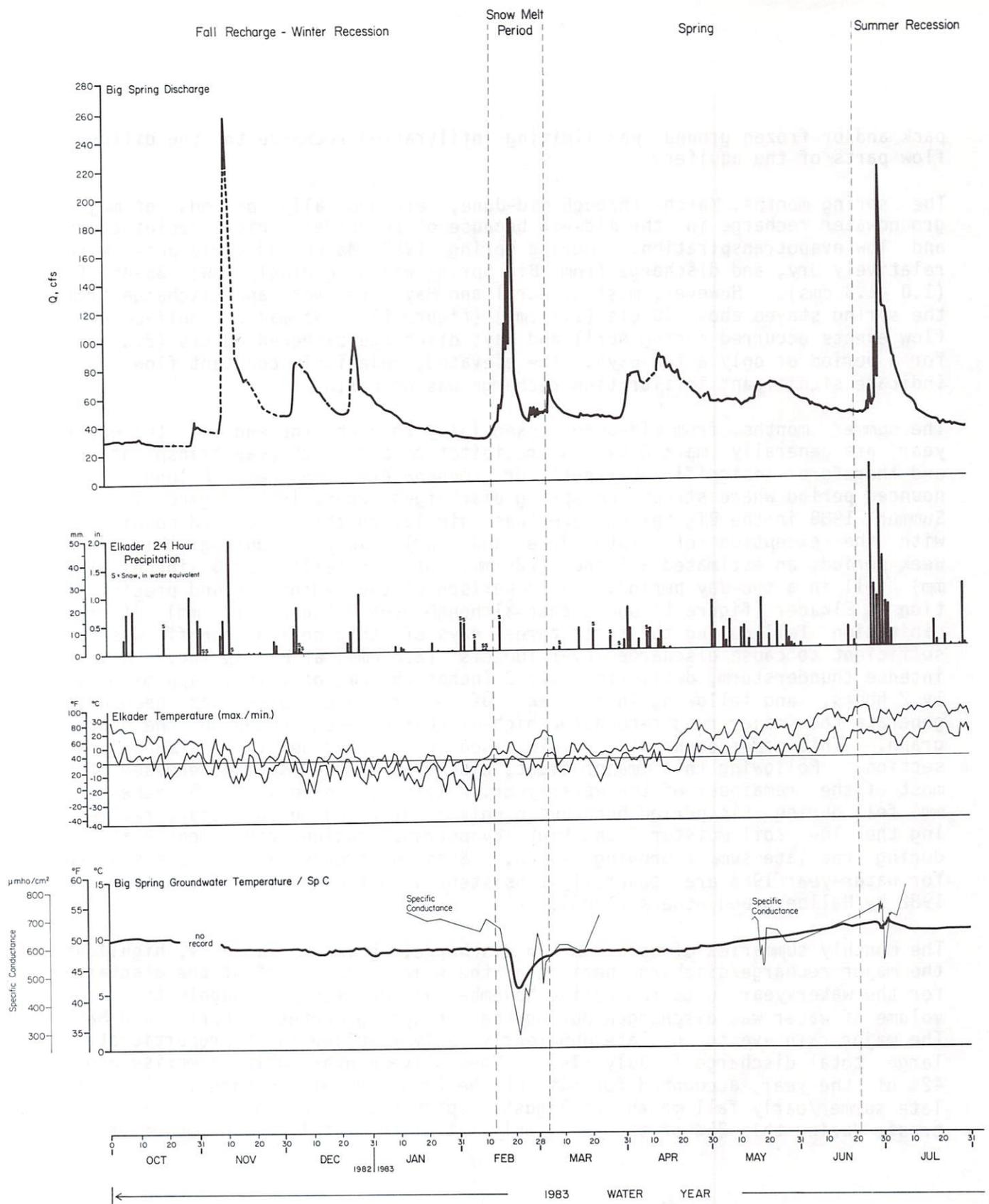


Figure 1. Discharge hydrograph from Big Spring; 24-hour precipitation, maximum and minimum daily temperatures, temperature and specific conductance of groundwater discharging at Big Spring, for Water-Year 1983.

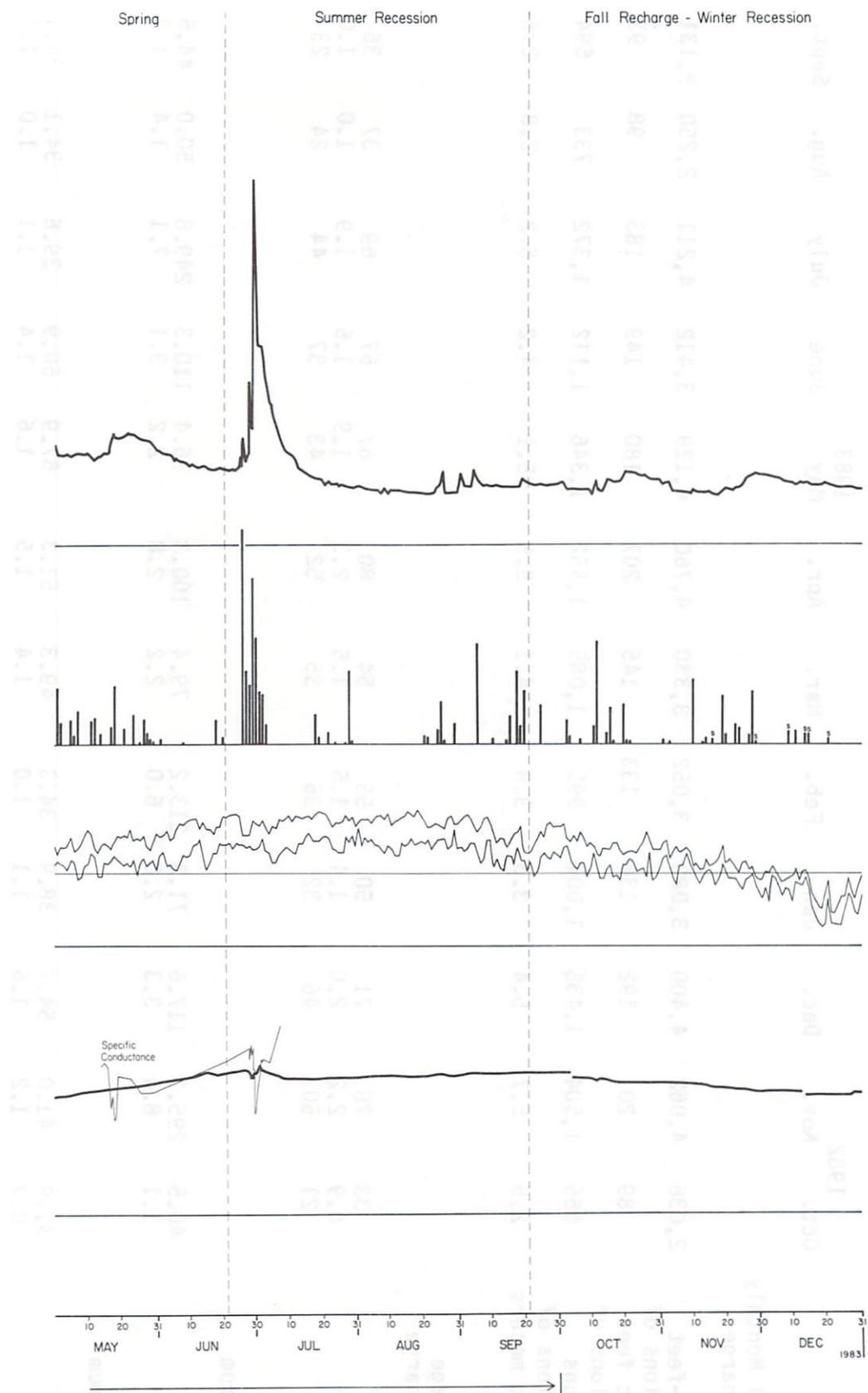


Figure 1. Continued. May through July overlaps with preceding page.

Table 4. Monthly summary of groundwater discharge data for the Big Spring basin for water-year 1983.

	1982					1983						
	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.
1. Total Monthly Discharge												
Acre-feet	2,038	4,062	4,400	3,080	3,052	3,330	4,760	4,129	3,412	4,211	2,250	2,131
Millions of cubic feet	89	201	192	134	133	145	207	180	149	183	98	93
Millions of gallons	666	1,504	1,438	1,004	995	1,085	1,552	1,346	1,112	1,372	733	694
Millions of cubic meters	2.5	5.7	5.4	3.8	3.8	4.1	5.9	5.1	4.2	5.2	2.8	2.6
2. Average Discharge												
cfs	33	78	71	50	55	54	80	67	57	69	37	36
cms	0.9	2.2	2.0	1.4	1.6	1.5	2.3	1.9	1.6	1.9	1.0	1.0
mg/d	21	50	46	32	36	35	52	43	37	44	24	23
3. Maximum												
cfs	40.5	295.3	117.6	71.3	213.2	79.4	100.3	76.4	110.3	249.8	50.0	44.5
cms	1.1	8.4	3.3	2.0	6.0	2.2	2.8	2.2	3.1	7.1	1.4	1.3
Minimum												
cfs	31.9	41.0	54.7	38.9	34.3	49.3	51.3	57.9	50.9	39.6	34.1	34.1
cms	0.9	1.2	1.5	1.1	1.0	1.4	1.5	1.6	1.4	1.1	1.0	1.0

and others (1983). Figure 2 shows total basin groundwater discharge, plotted on a semi-logarithmic scale, for ease of comparison to the discharge record from Turkey River. The Turkey River hydrograph shows daily discharge, in cfs, from the U.S.G.S. gaging station at Garber (#4125), 27 river miles downstream from Big Spring. The Turkey River drainage basin above Garber comprises 1545 square miles (4000 sq. km.), an area roughly 15 times the size of the Big Spring basin. The parallel nature of the Big Spring and Turkey River hydrographs is striking, and indicates that the responses noted in the Big Spring hydrologic system are typical of the much larger Turkey River drainage basin, and are likely typical of other "high" base-flow rivers in northeast Iowa (Hallberg et al., 1983).

Water Balance

From the various hydrologic data collected, a water balance was established for the Big Spring basin for water-year 1983.

Groundwater Balance

In its simplest form, a groundwater balance for the basin may be written in the following manner:

$$\text{Recharge} = \text{Discharge} + \Delta\text{Storage}$$

where, over the period of concern, recharge is all water entering the Galena aquifer, discharge is all water leaving the aquifer, and $\Delta\text{storage}$ is the change in the volume of water contained ("stored") within the aquifer.

Two major discharge mechanisms exist within the Galena aquifer. First, is the measured discharge to the Turkey River principally via Big Spring and associated springs. During water-year 1983, this amounted to 41,373 acre-feet (51 million m^3 ; Table 5). The other major mechanism is downward leakage to underlying aquifers, chiefly the St. Peter Sandstone (Hallberg et al., 1983). This was estimated to be approximately 10,000 acre-feet/year (12.3 million m^3) by Hallberg and others (1983). Groundwater withdrawals from wells in the area are negligible, relative to the above mechanisms.

Hallberg and others (1983) also describe the methods used for estimating storage changes within the aquifer. For water-year 1983, discharge from the basin was virtually the same at the beginning and end of the period, indicating no significant changes in storage water volume (figures 1 and 2).

Using the total estimated discharge and storage change volumes, recharge to the Galena aquifer within the basin may be calculated:

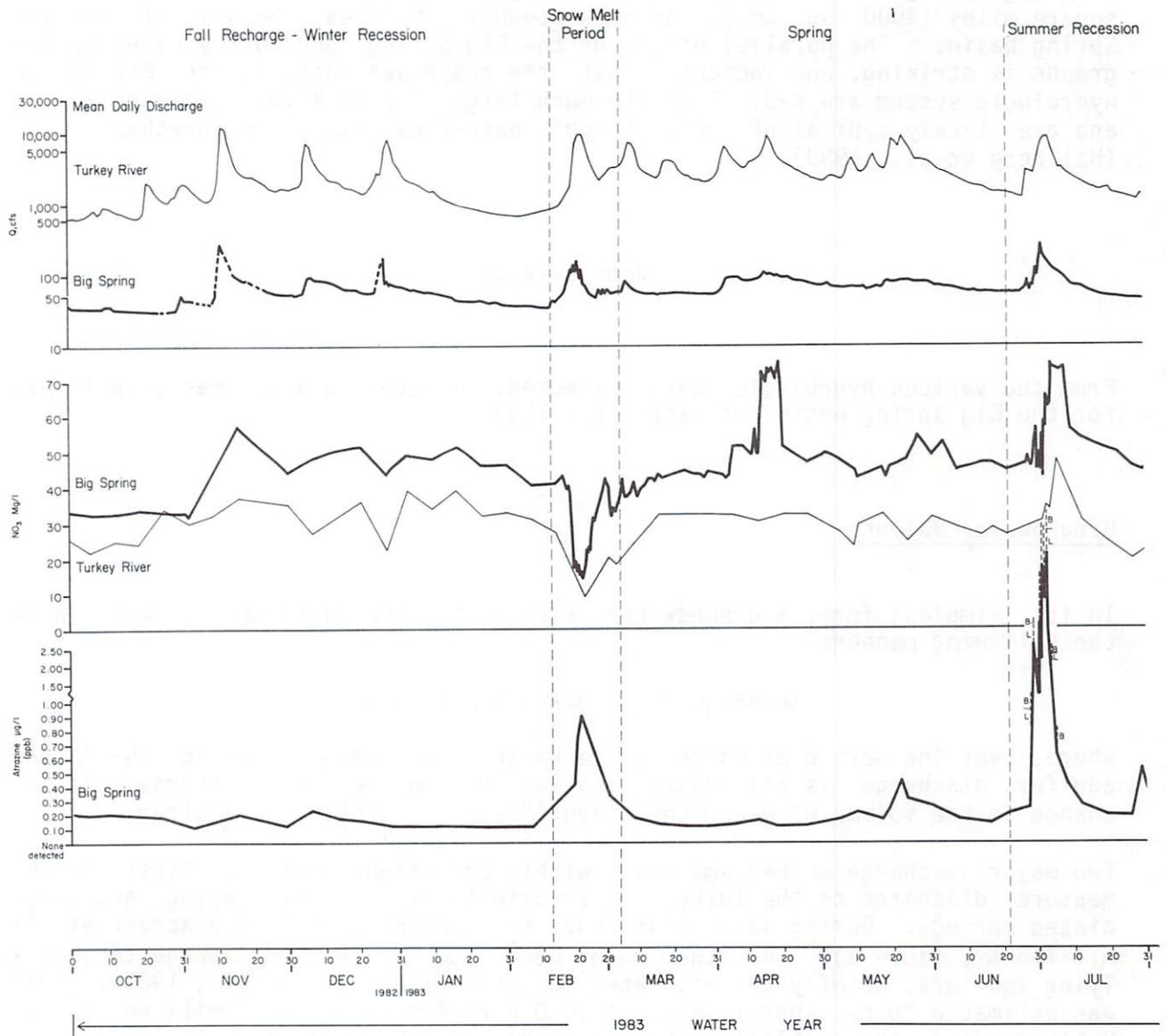


Figure 2. Discharge hydrographs from the Turkey River at Garber and the Big Spring groundwater basin; nitrate concentrations from the Big Spring and Turkey River; and atrazine concentration from Big Spring, for water-year 1983.

Recharge = Discharge + Storage
 = (41,373 acre-feet + 10,000) + 0 acre-feet
 = 51,373 acre-feet (53.3 million m³)

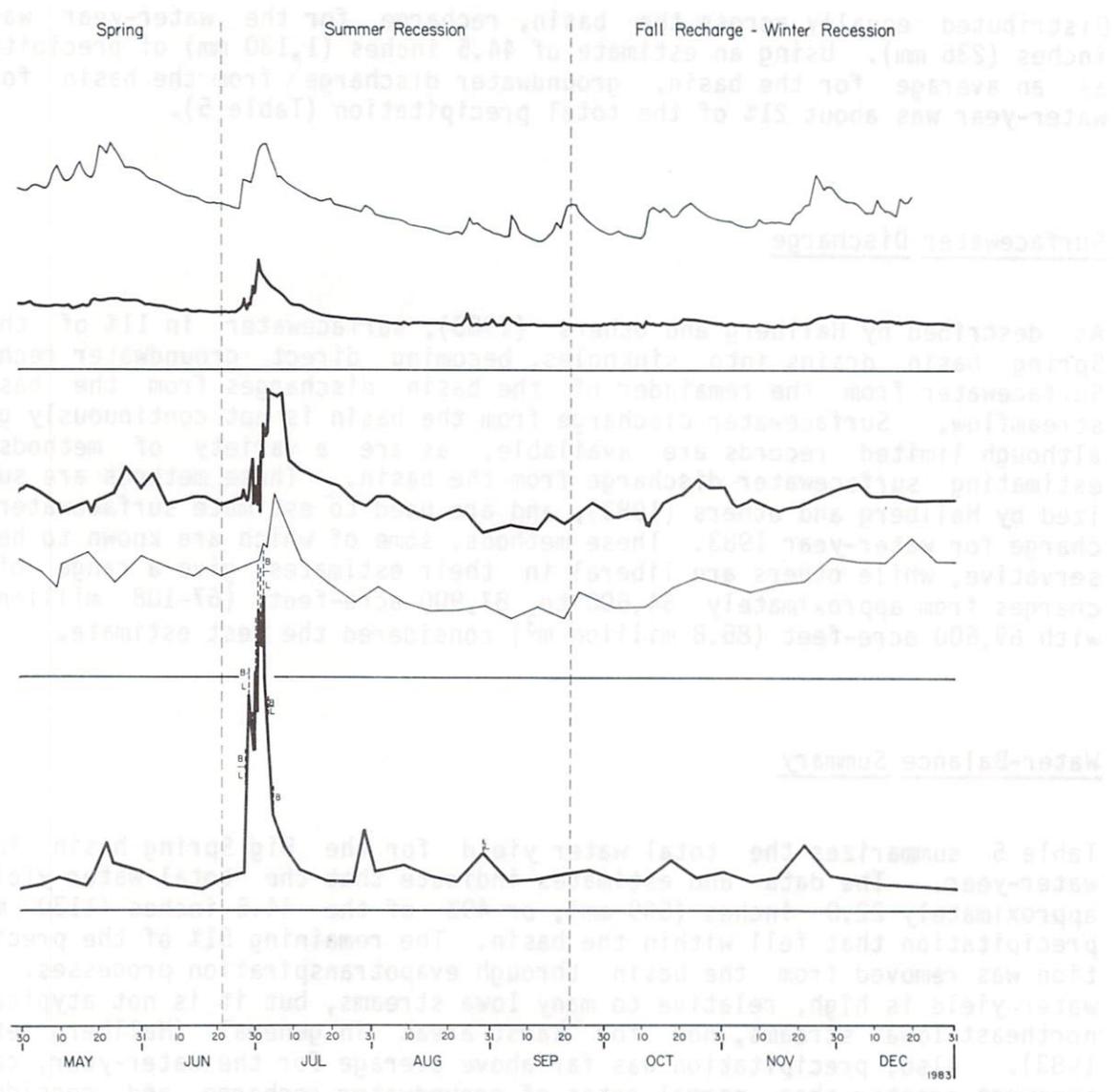


Figure 2, con't. May through July overlaps with preceding page.

$$\begin{aligned}
 \text{Recharge} &= \text{Discharge} + \Delta\text{Storage} \\
 &= (41,373 \text{ acre-feet} + 10,000) + 0 \text{ acre-feet} \\
 &= 51,373 \text{ acre-feet (63.3 million m}^3\text{)}
 \end{aligned}$$

Distributed equally across the basin, recharge for the water-year was 9.3 inches (236 mm). Using an estimate of 44.5 inches (1,130 mm) of precipitation as an average for the basin, groundwater discharge from the basin for the water-year was about 21% of the total precipitation (Table 5).

Surfacewater Discharge

As described by Hallberg and others (1983), surfacewater in 11% of the Big Spring basin drains into sinkholes, becoming direct groundwater recharge. Surfacewater from the remainder of the basin discharges from the basin as streamflow. Surfacewater discharge from the basin is not continuously gaged, although limited records are available, as are a variety of methods for estimating surfacewater discharge from the basin. These methods are summarized by Hallberg and others (1983), and are used to estimate surfacewater discharge for water-year 1983. These methods, some of which are known to be conservative, while others are liberal in their estimates, give a range of discharges from approximately 54,600 to 87,900 acre-feet (67-108 million m³), with 69,600 acre-feet (85.8 million m³) considered the best estimate.

Water-Balance Summary

Table 5 summarizes the total water yield for the Big Spring basin for the water-year. The data and estimates indicate that the total water yield was approximately 22.0 inches (559 mm), or 49% of the 44.5 inches (1130 mm) of precipitation that fell within the basin. The remaining 51% of the precipitation was removed from the basin through evapotranspiration processes. This water yield is high, relative to many Iowa streams, but it is not atypical for northeast Iowa streams, nor for karst areas in general (Hallberg et al., 1983). Also, precipitation was far above average for the water-year, causing somewhat greater than normal rates of groundwater recharge and, considerably more surfacewater runoff. For example, groundwater discharge from the Big Spring basin, as a percentage of rainfall, increased only 1% from water-year 1982 to water-year 1983 (see Hallberg et al., 1983) yet the total discharge increased 11%. For perspective the total water yield for the Turkey River for water-year 1983 was 19.63 inches, downstream at Garber, and 23.55 inches upstream at Spillville (and these figures would not include downward, groundwater leakage). The discharge for the 1983 water-year for the Turkey River at Garber was 1,617,000 ac-ft., an increase of 40% over water-year 1982.

Table 5. Total water yield from Big Spring basin for Water-Year 1983 (10/1/82 - 9/30/83).

	Acre-feet	(millions cubic meters)
GW discharge to Turkey River	41,373	(51.0)
GW leakage to St. Peter (change in storage)	10,000 0	(12.3) 0
Streamflow discharge	<u>69,600</u>	<u>(85.8)</u>
Total	120,973	(149.1)
Precipitation	44.5 inches	(1,130 mm)
Water Yield (less change in storage)	22.0 inches	(559 mm)
Water Yield as % of precipitation	49%	

WATER QUALITY MONITORING

As noted, a variety of water-quality parameters were monitored at Big Spring, the Turkey River, and at a number of stream, tile-line, and well sites within the basin during the 1983 water-year. The site locations are shown on figures 3 through 5. Figure 3 shows all the major sampling sites in the basin, and figures 4 and 5 show detailed maps of sampling sites in two sub-basins that drain to sinkholes. Particularly detailed sampling in the Bugenhagen basin (figure 4) will be discussed in later sections. As noted a variety of water quality parameters were measured. The water quality data from all these sites is tabulated, by site, in Appendix 1.

Nitrate Data From Big Spring

Nitrate concentrations from Big Spring are plotted on figure 2, along with the total basin groundwater hydrograph and data from the Turkey River. While there is not a simple, systematic relationship between discharges and nitrate concentrations, there are trends which show seasonal relationships that are essentially similar to the relationships previously discussed between precipitation, recharge, and discharge. The beginning of fall 1982 was a dry period

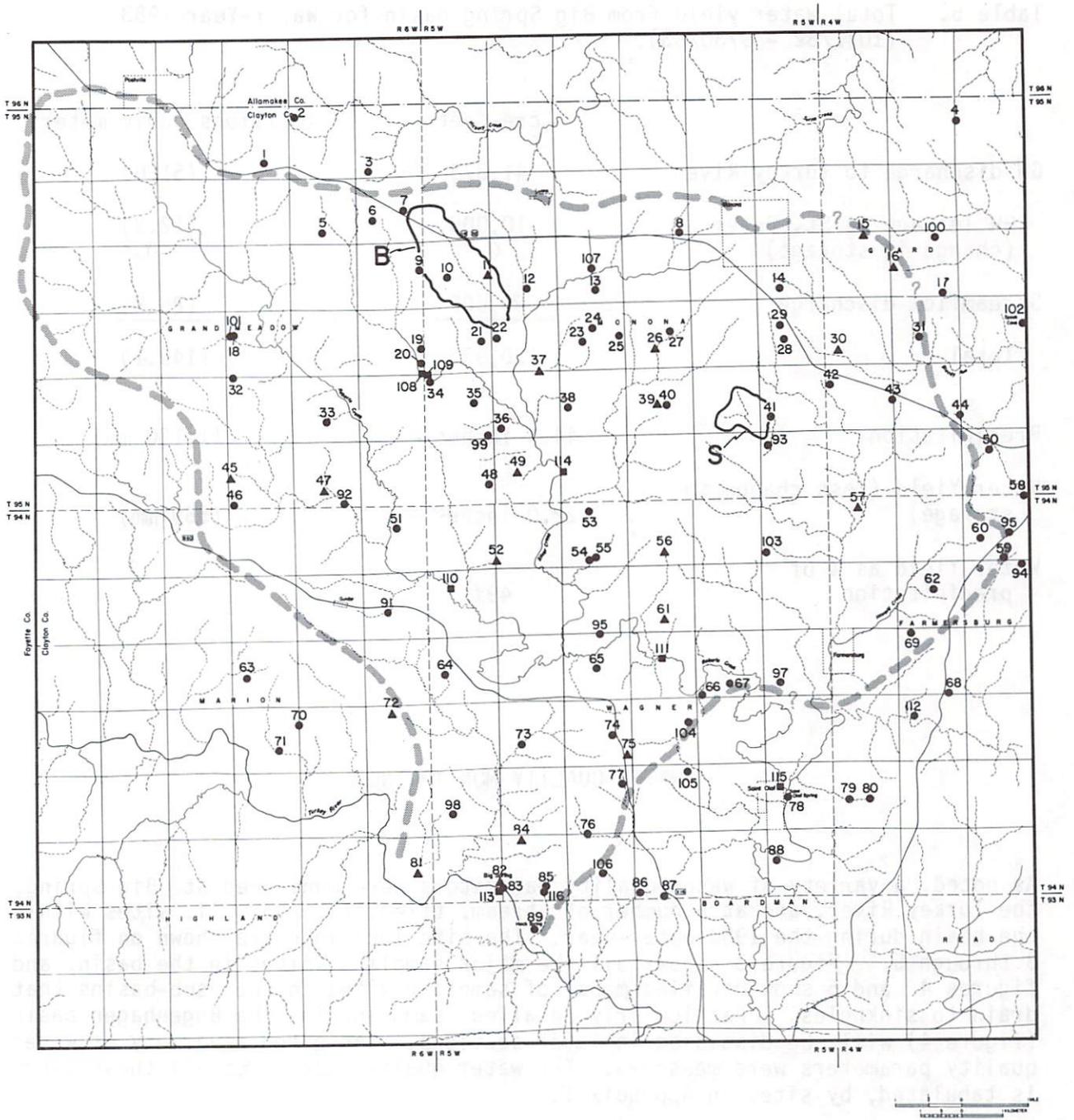


Figure 3. Water quality sample sites in Big Spring study area; circles are wells and springs; triangles are monthly network wells and springs from Hallberg et al., (1983); squares are surfacewater sites. Shaded areas indicate B-Bugenhagen basin on west, and S-Sass basin on east; details on figures 4 and 5. Shaded line outlines groundwater basin divide. Complete notations on all sites given in Hallberg et al. (1983).

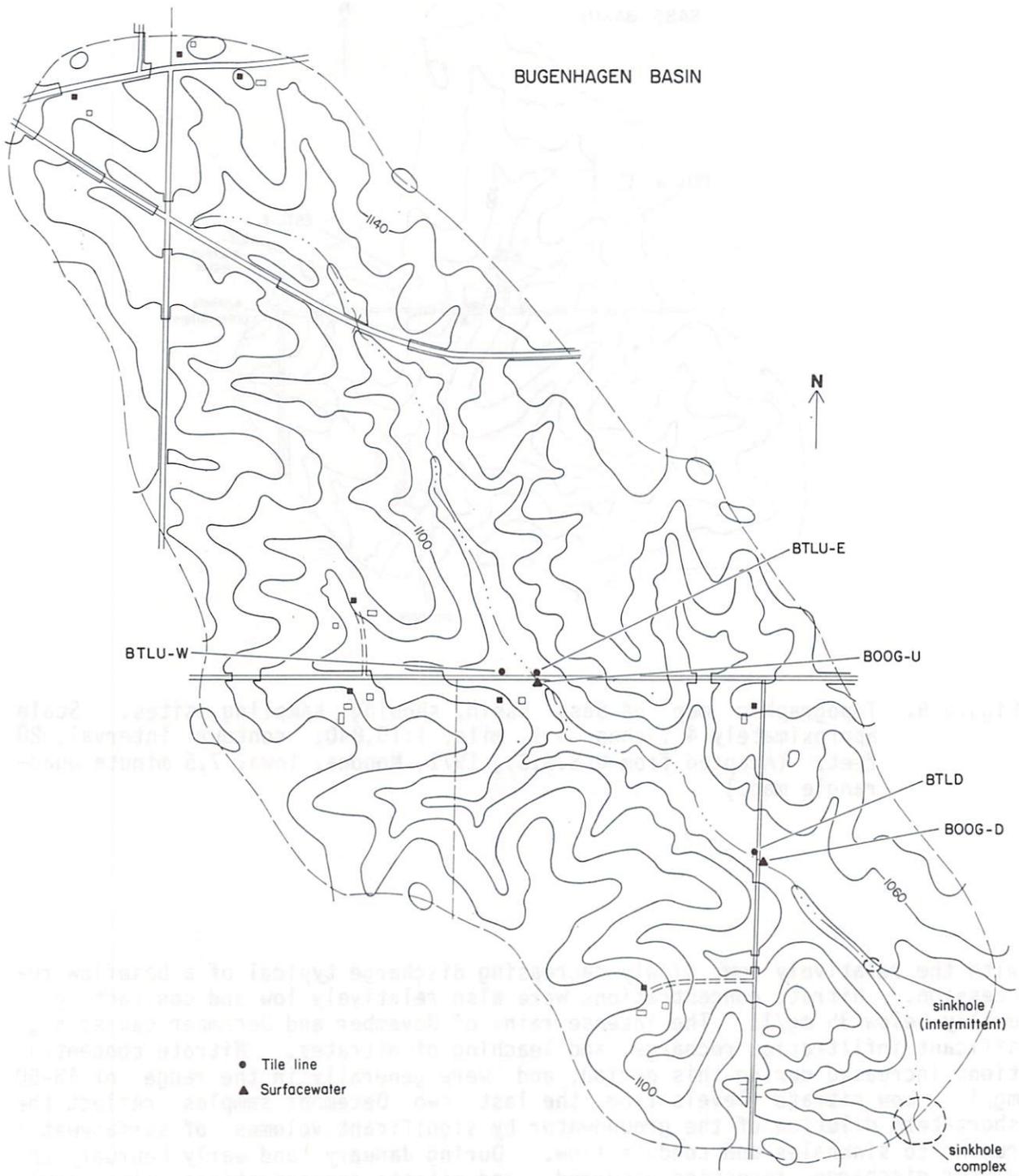


Figure 4. Topographic map of Bugenhagen basin, showing sampling sites. Scale approximately 4 inches = 1 mile; 1:15,840; contour interval, 20 feet. (Adapted from U.S.G.S., 1971, Monona, Iowa, 7.5 minute quadrangle map.)

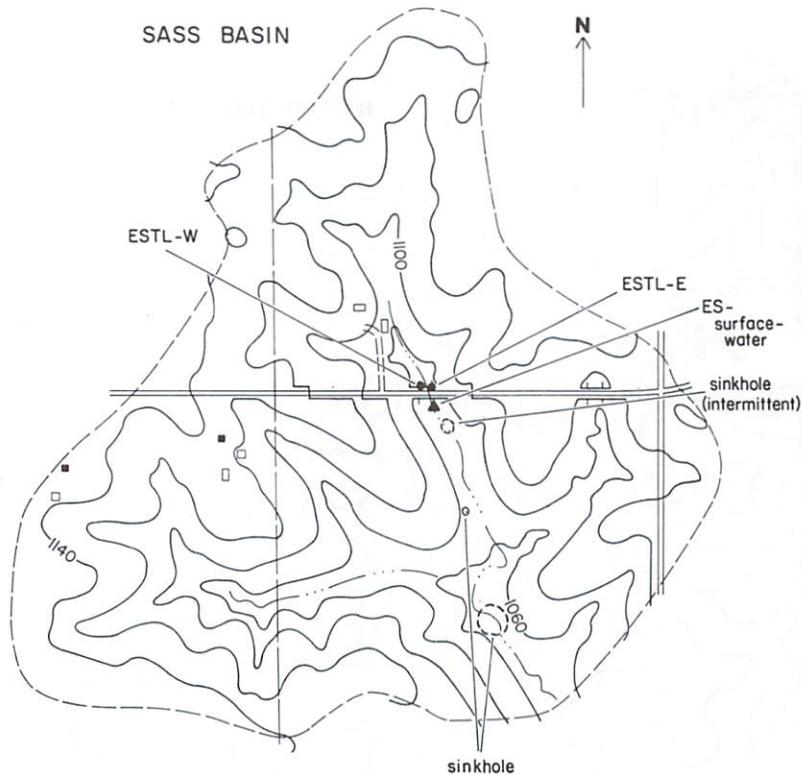


Figure 5. Topographic map of Sass basin, showing sampling sites. Scale approximately 4 inches = 1 mile; 1:15,840; contour interval, 20 feet. (Adapted from U.S.G.S., 1971, Monona, Iowa, 7.5 minute quadrangle map.)

with the relatively low, slowly decreasing discharge typical of a baseflow recession. Nitrate concentrations were also relatively low and constant, generally below 35 mg/l. The intense rains of November and December caused significant infiltration recharge, and leaching of nitrates. Nitrate concentrations increased during this period, and were generally in the range of 45-50 mg/l. Low nitrate levels from the last two December samples reflect the short-term dilution of the groundwater by significant volumes of surfacewater runoff to sinkholes and conduit flow. During January and early February the winter discharge recession occurred, and nitrate concentrations also slowly decreased to about 40 mg/l. During snowmelt, meltwater generated high discharges and very low nitrate concentrations. Nitrate levels dipped as low as 14 mg/l during peak conduit-flow periods; this is the lowest nitrate concentration yet observed at Big Spring since the current monitoring began in November 1981.

As discharge decreased after snowmelt, nitrate levels quickly returned to the 40-50 mg/l range for the month of March, which was relatively dry. Many minor rain events occurred during April and May, causing mainly infiltration recharge, rather than runoff, which generated nitrate levels of 45-50 mg/l for

much of the period. Prolonged, relatively high discharges (75-100 cfs; 2.1-2.8 cms) during mid-April, generated mainly by infiltration recharge again, apparently caused intense leaching of nitrates, pushing nitrate concentrations to 70-75 mg/l for about 1 week. At the beginning of this period nitrate levels increased from about 50 mg/l to over 70 mg/l in 24 hours, and nitrate concentrations decreased in an equally dramatic manner at the end of the period (figure 2). A similar response was observed following the very heavy rains and corresponding major discharge event which occurred in late June/early July. As the peak flows through the conduit system decreased and the discharge became dominated by infiltration-recharge, diffuse-flow, nitrate levels increased well above those preceeding the event, again reaching over 70 mg/l. Nitrate concentrations dropped rapidly a few days later. Intensive monitoring of discharge, nitrate levels, and other parameters during this period provide some evidence for the mechanism causing these rapid, dramatic increases and decreases in nitrate levels, and will be discussed in a later section.

During the remainder of the water year, no major recharge occurred, as indicated by the discharge hydrograph (figure 1). Nitrate levels generally decreased during this recession period, from about 45 to less than 40 mg/l (figure 2). Minor rains in late October (beginning water-year 1984) resulted in primarily infiltration recharge, and nitrate concentrations responded by climbing to over 50 mg/l.

The monitoring during the 1983 water-year substantiates the findings from water-year 1982. The same general seasonal relationships of nitrate concentrations and recharge are observed. Recharge occurs largely during the snowmelt-spring-early summer period, and again during the late fall-early winter period.

The magnitude of recharge during these periods is, of course, dependent on the amount of precipitation; hence, the difference observed between fall 1981 and fall 1982. During recharge periods, nitrate levels are high. During recession periods, which usually occur in late summer-early fall and again in winter, nitrate concentrations decrease. The highest nitrate concentrations occur during periods when large volumes of infiltration-recharge, diffuse-flow waters dominate the discharge. The lowest nitrate concentrations occur during recession periods, or when runoff, conduit-flow water dominates the discharge; the latter condition is most dramatically observed during snowmelt events.

Nitrate Data From the Monitoring Network

Nitrate concentrations from tile-line discharge water and various points along Roberts Creek, the major interior surfacewater drainage in the basin, are shown in figure 6 and 7 with data from Big Spring shown for comparison. Sites BTL-U and L22T (figure 6) are representative of the tile-line outlets which drain areas cropped to corn. Samples from these sites, which are indicative of the quality of infiltrating recharge waters, consistently show the highest levels of nitrates. Site L23S (figure 6) is a sampling point along a tributary to Silver Creek, located immediately downstream from where L22T discharges to the creek. The strikingly similar trends in nitrate concentrations

at these sites is clear, as is the similar trend of nitrate concentrations between these sites and Big Spring. Figure 7 shows nitrate levels at two other surfacewater monitoring points along Roberts Creek. Again, the same general trends in nitrate levels are observed across the water-year. Figure 8 shows nitrate levels from the Turkey River, with Big Spring for comparison. Although the drainage basin of the Turkey River is an order of magnitude larger than the Big Spring basin, weekly samples from the river and the spring indicate that even most small fluctuations in nitrate levels are coincident. The parallel nature of the nitrate records from the Big Spring, Roberts Creek, and the tile lines demonstrate that similar mechanisms and responses to recharge deliver nitrate to all parts of the Big Spring basin hydrologic system. The close coincidence of both the discharge (figure 2) and the nitrate records from Big Spring and the much larger Turkey River basin indicates that the recharge-discharge-nitrate concentration relationships documented at Big Spring operate on a regional scale. Comparison of these data with similar data for the Cedar River drainage basin, Devonian aquifer system in Floyd and Mitchell counties reinforces this conclusion (Libra et al., 1984), and suggests that the findings of the Big Spring investigations are generally applicable to all of the karst-carbonate terrane of northeast Iowa.

Nitrate-N Discharge

Table 6 summarizes the discharge of groundwater and nitrate-N in groundwater from the Big Spring basin to the Turkey River for the water year. The flow-weighted nitrate concentration from Big Spring was 46 mg/l; the mean of all analyses from the spring was 45 mg/l. These values indicate that average groundwater nitrate concentrations within the Galena aquifer in the basin were essentially at the concentration established as the nitrate drinking water standard by the U.S.E.P.A.

Total discharge of $\text{NO}_3\text{-N}$ in groundwater from the Big Spring basin to the Turkey River was 1.15 million lbs (522,000 kg)--approximately 575 tons of nitrogen. This amounts to a loss of nitrate-nitrogen of 17.4 lbs-N/acre (19.5 kg-N/ha) for the entire Big Spring basin.

Table 7 summarizes nitrate concentrations and the nitrate-N discharge on a monthly basis. As previously discussed, during the periods November-December, May-April, and July, 54% of the discharge for the water-year took place. Flow-weighted mean concentrations from these months were also above the annual flow-weighted mean. As a result, during this period, which is 42% of the year, 58% of the nitrate-N discharge occurred. During the low flow months of August, September, and October, flow-weighted mean nitrate concentrations were 42, 40, and 33 mg/l, respectively, which were below the annual mean. Only 16% of the total groundwater discharge occurred during this 25% of the water year, delivering only 13% of the total nitrate-N.

Table 8 summarizes the total water and nitrate-N discharged from the basin for the water-year. Total nitrate-N discharge is, in addition to the nitrate-N delivered to the Turkey River in groundwater (discussed above), comprised of nitrate-N carried by groundwater leaking downward to the St. Peter aquifer and

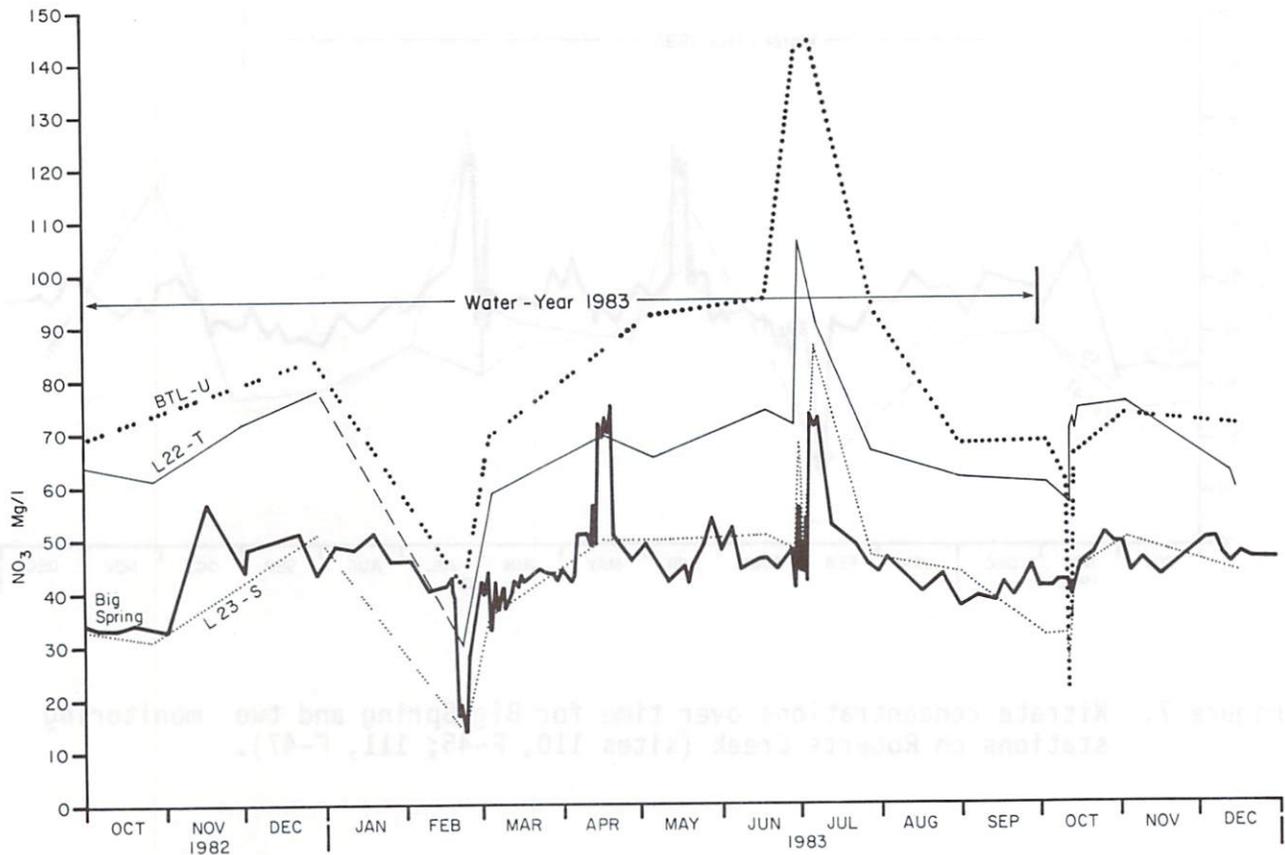


Figure 6. Nitrate concentrations over time for Big Spring, tile-line drainage water (sites 108, L22-T, and BTL-UW) and Silver Creek (site 109, L23-S.)

the nitrate-N discharged in surfacewater. Nitrate-N losses in leakage were about 203,000 lbs (92,000 kg). Total nitrate-N in surfacewater leaving the basin was about 1,514,000 lbs (687,000 kg) (the details of these calculations are given in Hallberg and others, 1983). Total nitrate-N discharged from the basin was, therefore, about 2,867,000 lbs (1,300,000 kg) --over 1,400 tons of nitrogen. This is equivalent to 43.3 lbs-N/acre (48.5 kg-N/ha) for the entire basin; 20.5 lbs-N/acre (22.9 kg-N/ha) in groundwater, and 22.8 lbs-N/ acre (25.6 kg-N/ha) in surfacewater.

Regional Nitrate-N Discharge from the Turkey River

Nitrate concentration and discharge were also monitored for the Turkey river. The mass of nitrate-N discharged by the Turkey River at Garber (drainage area 1,545 sq. miles; 2,486 sq. km) was about 26,865,000 lbs-N (12,102,000 kg-N)--over 13,400 tons of N. On an areal basis, for this regional basin, this amounts to approximately 27 lbs-N/acre (30 kg-N/ha) for the entire Turkey

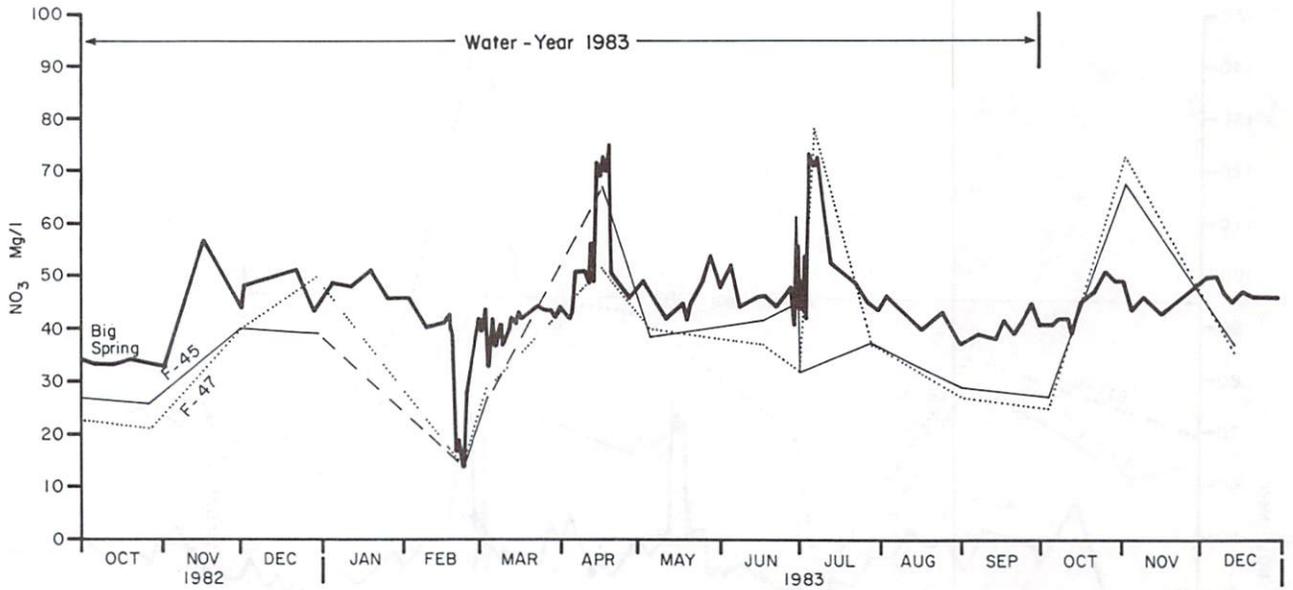


Figure 7. Nitrate concentrations over time for Big Spring and two monitoring stations on Roberts Creek (sites 110, F-45; 111, F-47).

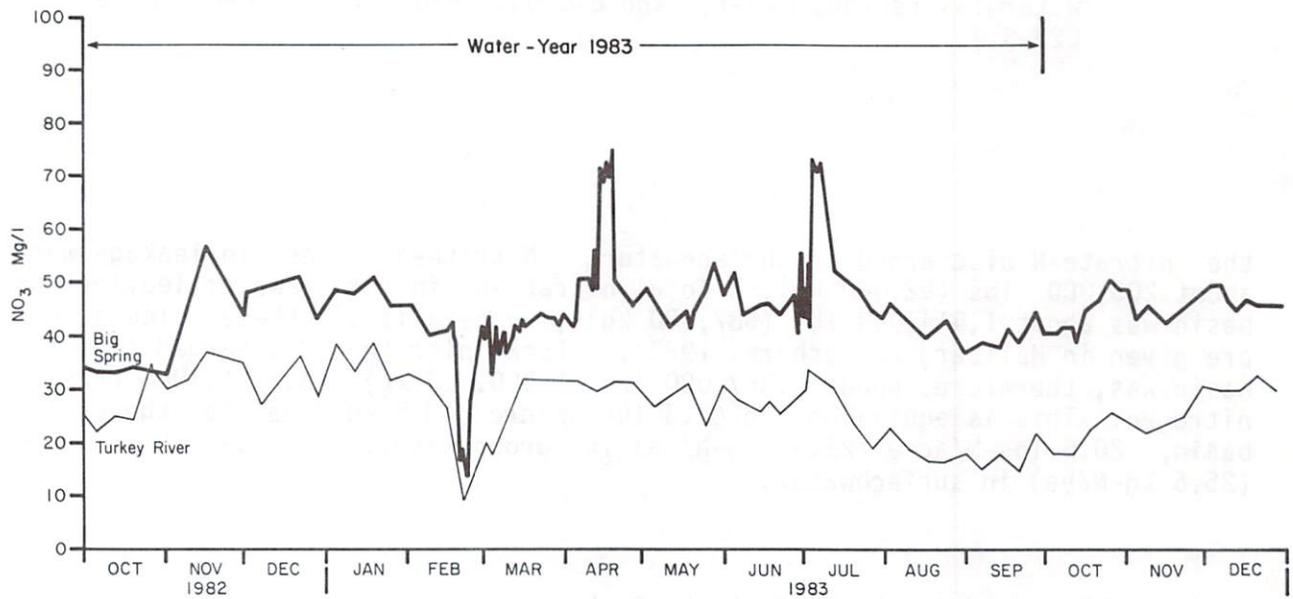


Figure 8. Nitrate concentrations for Big Spring and the Turkey River.

Table 6. 1983 Water-year summary of groundwater and chemical discharge from Big Spring basin to the Turkey River.

12-Month Summary; 10/1/82-9/30/83

1. Discharge

Total acre-feet	41,373
millions cf	1,802
millions cm	51.1
Average - cfs	70.9
cms	2.0
mg/d	46
gpm	31,820

2. Precipitation and Discharge

Precipitation	44.5 inches	(1,130 mm)
Discharge	9.3 inches	(236 mm)
Discharge as % of precipitation	21%	

3. Nitrate Discharge

Concentration--	
Flow-weighted mean	46 mg/l
Mean of analyses	45 mg/l
NO ₃ -N total output	
thousands lbs N	1,150
(thousands kg N)	(522)
lbs/acre of basin	17.4
(kg/ha of basin)	(19.5)

4. Atrazine discharge

Concentration--	
Flow-weighted mean	0.28 µg/l
Mean of analyses	0.72 µg/l
Total Output	
pounds	31.2
(kg)	(4.2)

Table 7. Monthly summary of nitrate-N output with groundwater discharged from the Big Spring basin to the Turkey River; 1983 water-year.

	1982							1983				
	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.
1. Flow-weighted mean NO ₃ concentration, in mg/l	33	47	47	48	33	41	54	47	47	56	42	40
2. Mean of NO ₃ analyses, in mg/l	33	45	47	49	26	40	57	46	47	55	42	41
3. Total monthly NO ₃ -N output												
Thousand lbs-NO ₃ -N	40	132	127	90	62	82	154	117	97	141	57	51
Thousands kg-NO ₃ -N	18	60	57	41	28	37	70	53	94	64	26	23

Table 8. Total water and nitrate yield from Big Spring basin for the 1983 water-year; 10/1/82-9/30/83.

1. Water Yield	Ac-ft		
A. Groundwater discharge to Turkey River	41,373		
B. Groundwater leakage (to St. Peter)	10,000		
C. Change in groundwater storage	(0)		
Total Groundwater Discharge (1A+1B)	51,373		
D. Streamflow discharge	69,600		
Total Water-Yield	120,973 Ac-ft		
2. Precipitation and Discharge			
A. Precipitation	44.5 inches (1,130 mm)		
B. Water Yield, less change in gw storage	22.0 inches (559 mm)		
C. Water yield (as 2B) as % of precipitation	49%		
3. N-discharge	Thousands Pounds-N (Thousands kg-N)		
A. NO ₃ -N, gw output to Turkey River	1,150 (522)		
B. NO ₃ -N, gw leakage	203 (92)		
NO ₃ -N output in groundwater	1,353 (614)		
C. NO ₃ -N, in surfacewater discharge	1,514 (687)		
Total NO ₃ -N output	2,867 (1,300)		
	Total	GW	SW
D. lbs-N/acre of basin (kg-N/ha of basin)	43.3 (48.5)	20.5 (22.9)	22.8 (25.6)

River basin. In considering losses to agriculture, this is a minimum value in many respects, because it does not include the other forms of N that are lost in the Turkey River water, it does not account for in-stream N-use or gaseous losses, and because the acreage figure includes all the land areas, e.g., forested area as well as cropland. This compares favorably with the 43 lbs-N/ac (49 kg-N/ha) calculated for the Big Spring basin. Also, the ratio of N-loss/ac, between the Big Spring basin and the Turkey River basin was very similar for water-years 1982 and 1983 (1.4 and 1.6). Again, this suggests that the results and conclusions from Big Spring are clearly useable on a regional basis in Iowa.

Pesticide Monitoring - Big Spring

Samples for pesticide analysis were collected from Big Spring on a weekly to bi-weekly basis during the water-year. More intensive sampling was carried out during high discharge events. Results are plotted on figure 2. Atrazine is the most commonly detected pesticide found in the springs's discharge. Other species detected during the water-year, usually during high-discharge events, include Bladex (cyanazine), Lasso (alachlor), Dual (metolachlor), and Dyfonate (fonofos). Dieldrin (an insecticide no longer in use) was detected, attached to sediment/organic particulates discharged from the spring. The results of all pesticide analyses from Big Spring are tabulated on Table 9 (and in Appendix 1).

During the beginning of the water-year, until snowmelt occurred in mid-February, atrazine concentrations were generally between 0.1 and 0.2 $\mu\text{g/l}$, falling to a constant 0.1 $\mu\text{g/l}$ during the winter baseflow recession. Occasional samples showed minor increases, possibly related to the major fall rains. However, sampling was not sufficiently detailed during this period to isolate these major storms. Melting of the winter snowpack in February delivered surface-runoff/runin recharge to the aquifer. Atrazine concentrations increased during this period, reaching 0.85 $\mu\text{g/l}$. Atrazine levels decreased after the snowmelt period, and, with minor exceptions, did not exceed 0.2 $\mu\text{g/l}$ until mid-May. Atrazine concentrations of 0.1 -0.2 $\mu\text{g/l}$, therefore, may be considered as the average background level in Big Spring discharge, during periods when insignificant runoff recharge occurs and baseflow discharge is dominant. Late spring and summer rains, particularly in May and late June/early July, caused a series of minor to major runin-recharge, conduit-flow events. These events were monitored closely for discharge and chemical water-quality parameters. Pesticide monitoring indicated the presence of atrazine, Bladex, Lasso, Dual, and Dyfonate. Maximum concentrations of the above chemicals during this period were: Atrazine, 5.1 $\mu\text{g/l}$; Bladex, 1.2 $\mu\text{g/l}$; Lasso, 0.63 $\mu\text{g/l}$; Dual 0.62 $\mu\text{g/l}$; and Dyfonate, 0.11 $\mu\text{g/l}$. (Details of the monitoring during this period will be presented in a later section.) These elevated levels decreased rapidly as the conduit-flow discharge receded. During the remainder of the water-year, only minor runoff recharge events occurred and with a few exceptions, atrazine was the only pesticide detected at Big Spring, persisting at concentrations of 0.1-0.2 $\mu\text{g/l}$.

Table 9. Results of UHL analyses for pesticides in water and sediments from Big Spring.

<u>Date</u> <u>Time</u>	<u>Analysis</u> $\mu\text{g/l}$ (ppb)	<u>Atrazine</u>	<u>Bladex</u>	<u>Lasso</u>	<u>Dual</u>	<u>Dyfonate</u>
Water Year 1982						
10/27/81	N.D. in water, or sediments in raceway.					
11/10/81	N.D. in water, or sediments in raceway.					
12/15/81	N.D. in water.					
2/25/82	N.D. in water (or any wells or surfacewater).					
3/22/82	N.D. in water; 0.65 Dieldrin in sediments collected from spring.					
5/12/82		0.18				
5/18/82		0.44		0.15		
5/27/82		0.8	0.2			
5/28/82		2.5	0.15			
6/01/82		0.4	0.07			
6/08/82		0.26				
6/15/82		0.45	0.08	0.08		
6/23/82		0.70	0.09	0.05		
6/29/82		0.75	0.07			
7/06/82		0.49				
7/07/82		0.49				
7/08/82		0.45				
7/13/82		0.31				
7/21/82		0.63				
7/28/82		0.62				
8/03/82		0.55				
8/25/82		0.26				
9/07/82		0.30				
9/22/82		0.28				
Begin Water Year 1983						
10/05/82		0.19				
10/12/82		0.20				
10/26/82		0.18				
End Water Year 1982 (See Text for Explanation)						
11/03/82		0.10				
	(sediment-3.6 Dieldrin; 5.1 Atrazine)					
11/16/82		0.19				
11/30/82		0.11				
	(sediment-1.1 Dieldrin; 5.0 Atrazine)					
	(sediment-8.0 Dieldrin)					
12/07/82		0.22				
12/14/82		0.17				
12/21/82		0.16				
12/28/82		0.12				

Table 9. Cont'd.

Date Time	Analysis $\mu\text{g/l}$ (ppb)	Atrazine	Bladex	Lasso	Dual	Dyfonate
12/29/82		0.11				
1/04/83		0.11				
1/11/83		0.12				
1/18/83		0.12				
1/25/83		0.10				
2/08/83		0.11				
2/20/83						
8:30am		0.41				
2/21/83						
8:20am		0.67				
7:15pm		0.72				
2/22/83						
9:15am		0.88				
	(9.2 Atrazine in sediment)					
3/01/83		0.32				
3/08/83		0.16				
3/15/83		0.12				
3/22/83		0.11				
3/29/83		0.10				
4/05/83		0.14				
4/12/83		0.16				
4/19/83		0.10				
4/26/83		0.10				
5/05/83		0.15				
5/10/83						
8:30am		0.21				
5/17/83		0.15	0.15	0.08		
5/18/83		0.21				
5/19/83		0.23	0.15	0.24		
5/22/83		0.42	0.19	0.32		
5/24/83		0.29	0.08	0.09		
5/31/83		0.24				
6/07/83		0.16				
6/17/83		0.13				
6/22/83		0.18				
6/27/83						
5:00pm		0.23				
6/28/83						
11:25am		0.80	0.19	0.11		
5:30pm		2.50	0.10	0.60	0.41	
6/30/83						
12:30am		1.40	0.29	0.32		
10:40am		1.10	0.32	0.28		
4:00pm		1.90	0.69	0.47		
10:20pm		3.10	1.00	0.45		

Table 9. Cont'd.

Date Time	Analysis $\mu\text{g/l}$ (ppb)	Atrazine	Bladex	Lasso	Dual	Dyfonate
7/01/83						
6:00am		1.60	0.36	0.38		
9:30am		2.10	0.19	0.28		
11:30am		2.30	0.76	0.39		
1:50pm		2.10	0.62	0.36	0.62	
6:00pm		4.70	0.43	0.63		
10:20pm		3.80	1.20	0.62	0.25	0.11
7/02/83						
1:30am		5.10	0.71	0.57		
		(2.6 Atrazine and 0.6 Dieldrin in sediment)				
9:45pm		2.0	0.24	0.19		
7/05/83						
4:30pm		0.58	0.21			
7/08/83		0.42				
7/12/83		0.25				
7/19/83		0.18				
7/26/83		0.17				
7/29/83		0.51				
8/02/83		0.24				
8/09/83		0.27				
8/16/83		0.21				
8/23/83		0.18				
8/30/83		0.35		0.11		
9/06/83		0.18				
9/13/83		0.19				
9/20/83		0.22				
9/27/83		0.24				
10/03/83		0.19				
10/04/83		0.19				
10/11/83						
1:10pm		0.18				
10/12/83						
8:00am		0.20				
10/18/83		0.32				
10/25/83		0.20				
End Water Year 1983						
11/01/83		0.24				
11/08/83		0.18				
11/15/83		0.21				
11/22/83		0.42				
11/29/83		0.22				
12/06/83		0.19				
12/13/83		0.16				
1/04/84		0.13				

Atrazine Discharge

The mass of atrazine discharged from Big Spring can be calculated in the same fashion as nitrate-N discharge. The total atrazine output in groundwater discharged from the basin (Table 6) during the water year was 31.2 lbs (14.2 kg). The flow-weighted mean concentration in groundwater was 0.28 $\mu\text{g}/\text{l}$, while the mean of all analyses was 0.72 $\mu\text{g}/\text{l}$. These means for atrazine do not correspond as well as those for nitrate. This is a reflection of the fewer number of samples collected, and the fact that the most intensive sampling for pesticides was done during runin, conduit-flow periods when the highest concentrations of pesticides occur.

As in water-year 1982 the number of surfacewater analyses for pesticides was not sufficient to allow for the calculation of the amount of pesticides discharged in surfacewater. However, as discussed by Hallberg and others (1983) the concentrations of pesticides in surfacewater generally range from 10 to 100 times greater than those found in groundwater. Even at this rate the mass of pesticides discharged with the water from the basin is small, and is estimated at about 5% of that applied.

Hydrograph Separations: Runin and Infiltration Components of Groundwater Discharge

The total basin, groundwater hydrograph was separated into diffuse-flow or base-flow (infiltration) and conduit-flow (surfacewater runin) components, using the methods described in Hallberg and others (1983). The values given here are based on methods modified from Singh and Stall (1970), as outlined by Hallberg and others (1983). Estimates were made of the mass and mean concentration of nitrate and atrazine carried in these components, from the detailed analyses of various discharge events. The significance of these flow components, their recharge mechanisms, the relationship between recharge mechanisms and chemical mobilization, and their implications for agricultural management practices are discussed in Hallberg and others (1983). Further description and verification of the applicability of these methods will be discussed in the section on particular discharge events, later in this report.

Table 10 summarizes the results of the hydrograph separations. Base flow during the water-year was about 37,00 acre feet (45.5 million m^3), 89% of the total discharge. The remaining 11%, or 4,500 acre-feet (5.6 million m^3) was discharged as peak-conduit flows following major rainstorms and the spring snowmelt.

Base flow carried with it approximately 1.1 million pounds (500,000 kg) of nitrate-N or 95% of the total nitrate-nitrogen discharged for the water-year. The flow-weighted mean nitrate concentration in baseflow was 49 mg/l . Peak conduit-flows delivered about 57,000 lbs (26,000 kg) of nitrate-N, at an average, flow-weighted nitrate concentration of 22 mg/l . Base flow shows an enrichment in nitrate, relative to conduit flows, because nitrate is mobilized by groundwater infiltrating through the soil horizons, where the nitrate is

stored. Surface runoff that enters the groundwater via sinkholes ("runin" water) dilutes the nitrate concentration in water discharging from Big Spring; this is particularly true in runoff generated by melting snow.

Base flow discharge to the Turkey River delivered about 16.7 lbs (7.6 kg) of atrazine; about 53% of the total atrazine load for the water-year. The flow-weighted mean concentration of atrazine in baseflow was 0.16 $\mu\text{g}/\text{l}$. Conduit flows carried the remaining 14.5 lbs (6.6 kg) of atrazine, at an average, flow-weighted concentration of 1.20 $\mu\text{g}/\text{l}$. This is consistent with the previous observations (see Hallberg et al., 1983) that indicate atrazine, and other moderately adsorbed pesticides, are enriched in surface runoff, relative to the infiltrating water that supplies baseflow to the spring.

As noted by Hallberg and others (1983) and Libra and others (1984), although the runin, conduit-flow component carries the greatest concentrations of pesticides into the groundwater system, the base flow, or infiltration component still delivers the majority of the soluble pesticides into the groundwater system, over the course of a water-year.

Comparison of 1982 and 1983 Water-Years

A comparison of the data for the two complete water-years of monitoring provides some interesting perspectives. The data are summarized on Table 11.

Precipitation was above average in both water-years (WY), but in WY-1983 was 31% more than in WY-1982. As a consequence, the water-yield for the water-year increased approximately 47% (67% if changes in groundwater storage are subtracted); with streamflow discharge about twice (100% increase) that of WY-1982, and the groundwater discharge (disregarding discharge from storage) increasing 37%.

The change in groundwater storage in WY 1982 cannot be removed easily from the components of groundwater discharge or from the chemical discharge figures. Thus, total figures are shown on Table 11. Runin-conduit flow increased significantly (34%), as would be expected from the large increases in streamflow recorded in WY-1983. If the total change in storage for WY-1982 is removed from infiltration-base flow, then this component would show an increase of 52% in WY-1983.

Total $\text{NO}_3\text{-N}$ discharged from the Big Spring basin also increased substantially (58%); the equivalent lost from the basin increasing from approximately 27 lbs-N/acre (20 kg-N/ha) to over 43 lbs-N/acre (48 kg-N/ha). This increase results from two inter-related factors: 1) the large increase in water discharged; and 2) the increase in the nitrate concentration in the groundwater recorded in WY-1983.

The nitrate concentration in streamflow was essentially the same in WY-1982 and WY-1983. Thus, the increase in $\text{NO}_3\text{-N}$ discharged is proportional to the increased volume of water discharged. For the groundwater, however, the flow-weighted mean concentration increased 18%, from 39 mg/l to 46 mg/l. As shown

Table 10. Components of groundwater and chemical discharge for water-year 1983, from Big Spring basin to Turkey River.

Water-Year 10/1/82-9/30/83

1. Discharge

Conduit (Runin) Flow	
acre-feet	4,502
millions cf	196
millions cm	5.6
% total	11%

Base (Infiltration) Flow	
acre-feet	36,871
millions cf	1,606
millions cm	45.5
% total	89%

2. Nitrate Output

Peak Conduit Flow; NO ₃ -N (flow-weighted mean NO ₃ -22 mg/l)	
thousand lbs	57
(thousand kg)	(26)
% total	5%

Base Flow; NO ₃ -N (flow-weighted mean NO ₃ -49 mg/l)	
thousand lbs	1,093
(thousand kg)	(496)
% total	95%

3. Atrazine Output (5/6/82-10/31/82)

Peak Conduit Flow	
Flow-weighted mean concentration	1.20 µg/l
Total pounds	14.5
(Total kg)	(6.6)
% Total	47%

Base Flow	
Flow-weighted mean concentration	0.16 µg/l
Total pounds	16.7
(Total kg)	(7.6)
% Total	53%

on figure 9, there were few comparable periods when the nitrate concentration in groundwater was not greater in WY-1983 than in WY-1982.

Similar changes are noted regionally as well. Total water yield to the Turkey River increased 40 % at Garber and 71% at Spillville. Nitrate-N discharged from the Turkey River basin at Garber increased 42%, from an equivalent of 19 lbs-N/ac (21 kg-N/ha) to 27 lbs-N/ac (30kg-N/ha).

The amount of atrazine discharged in groundwater from the basin, while still quite small compared to $\text{NO}_3\text{-N}$, increased even greater proportionally--120% from WY-1982 to WY-1983. The atrazine discharged in the runin-conduit flow component increased 530%; most of which occurred during the peak discharges of late June-early July. Of more general significance is the 40% increase in atrazine discharged in the infiltration-base flow component. This occurred even though the flow-weighted mean atrazine concentration was similar. Most of this increase occurred because atrazine was present in the groundwater year-round in WY-1983, while in WY-1982 it was not detected during the fall and winter recession period. In addition, more pesticide species were detected in groundwater in WY-1983, and the highest concentrations of each detected pesticide occurred at Big Spring in WY-1983 (Table 12). The occurrence of pesticides, other than atrazine, in the groundwater at Big Spring was still common only during periods related to runin-conduit flow. However, some of these pesticides have also been detected year-round in groundwater in Floyd and Mitchell counties (Libra et al., 1984).

For perspective, only a very few of the pesticides used in the area have been detected in the groundwater (compare Tables 12 and 2). However, those found in groundwater are, by far, the most commonly used pesticides in the basin. Also, the analyses have only been for the parent products; no analyses have been performed which might identify metabolites or breakdown products of other pesticides.

These substantially greater losses of agriculturally-used chemicals occurred despite the significant reductions in total application of fertilizer-N and pesticides (primarily because of decreased corn-acreage) which took place because of the PIK program. This should be expected, however. It takes time for the soil-groundwater system to respond. Significant amounts of these chemicals are stored in the soil-water system, related to leaching losses below the root zone over many years (this will be further discussed in later sections dealing with soil sampling). These chemicals remain in storage, only to be mobilized and displaced during subsequent infiltration events. It will take some amount of time before the effects of PIK are measureable (if such a one-year change is measureable!). Figures 10 and 11 help to emphasize this point. They show a plot of total groundwater discharge on a monthly basis, versus the flow-weighted mean nitrate concentration in groundwater and total load of $\text{NO}_3\text{-N}$ discharged in the groundwater for that month. Some seasonal groupings are apparent, and excluding March of 1982, which was dominated by snowmelt runin - dilute in nitrate - significant simple linear relationships are apparent. Both data sets show simple linear regression relationships significant at the 0.001 level (using SAS and ANOVA statistical packages).

Total load versus total discharge (figure 11) shows a stronger relationship because the $\text{NO}_3\text{-N}$ load is the product of the concentration and water discharge (but on a daily basis). However, this still serves to normalize the data to a

Table 11. Comparison of total water and chemical discharge from the Big Spring basin for 1982 and 1983 water-years (1982 data from Hallberg et al., 1983).

	Water-year		Percentage ¹ Change
	1982	1983	
1. Water Yield			
<u>Total Groundwater discharge</u>	47,400 (58.5)	51,373 (63.4)	+8%
Groundwater discharge, less change in storage	37,400 (46.1)	51,373 (63.4)	+37%
Streamflow discharge	34,750 (42.9)	69,600 (85.9)	+100%
Total Water Yield	82,150 (101.3)	120,973 (149.2)	+47%
2. Precipitation and Discharge			
<u>Precipitation</u>	34 in (864 mm)	44.5 in (1130 mm)	+31%
Water Yield (less change in groundwater storage)	13 in (332 mm)	22 in (559 mm)	+69%
Water yield as % of precipitation	38%	49%	
3. Components of groundwater discharge to the Turkey River <u>Acre/feet (millions cubic meters)</u>			
Runin - Peak Conduit Flow	3,360 (4.1)	4,502 (5.6)	+34%
Infiltration - Base Flow	34,040 (42.0)	36,871 (45.5)	+8%
4. Nitrate-N Discharge			
<u>Flow-weighted mean NO₃ concen- tration in groundwater</u>	39 mg/l	46 mg/l	+18%
	Thousand pound-N (Thousands kg-N)		
NO ₃ -N discharged in surfacewater	1,053 (478)	1,353 (614)	+28%
NO ₃ -N discharged in groundwater	756 (343)	1,514 (687)	+100%
Total NO ₃ -N discharged	1,809 (821)	2,867 (1,300)	+58%
lbs-N/acre of basin (kg-N/ha of basin)	27.4 (30.7)	43.3 (48.5)	+58%
5. <u>Atrazine Discharged in Groundwater</u>			
	Pounds (kg)		
In Runin-Peak Conduit Flow	2.3 (1.1)	14.5 (6.6)	+530%
In Infiltration-Base Flow	11.9 (5.4)	16.7 (7.6)	+40%
Total Atrazine Discharged	14.2 (6.5)	31.2 (14.2)	+120%

¹ $\frac{(\text{Difference between 1982 and 1983 values}) \times 100}{1982 \text{ value}}$

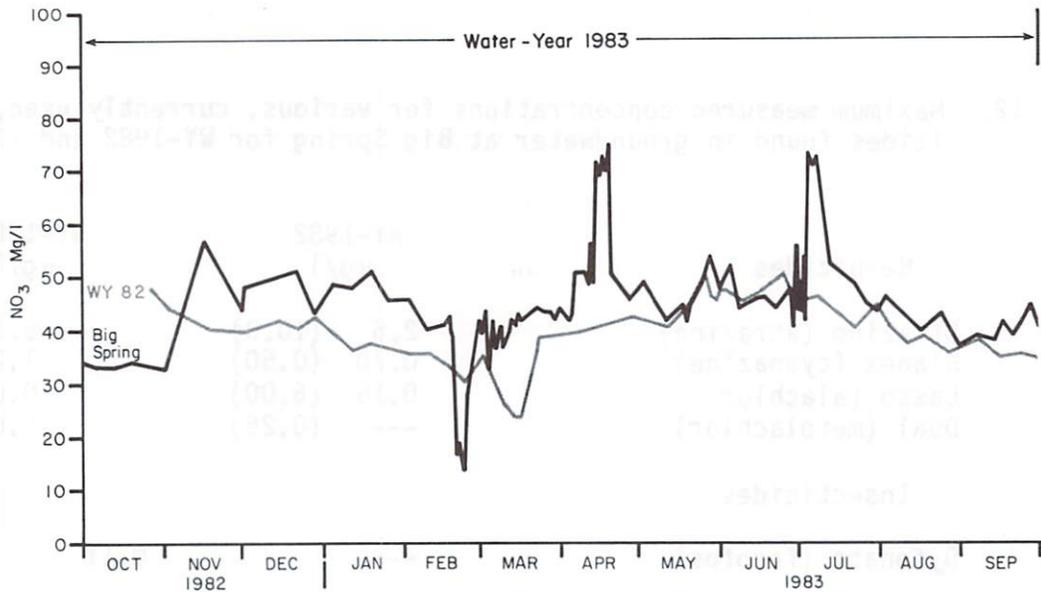


Figure 9. Comparison of nitrate concentrations at Big Spring for 1983 (black) and 1982 (gray) water-year.

common frame of reference. Excluding March 1982 the r^2 for these data (figure 11) is 0.94. As discussed, 90-95% of the discharge from Big Spring is from infiltration-base flow or the diffuse-flow component. The inference from such a strong relationship is that the amount of $\text{NO}_3\text{-N}$ discharged over these two water years is essentially a function of how much water was flushed, or displaced, through the soil-water system into the groundwater. This is logical; as more water infiltrates through the soil it would more effectively and efficiently displace NO_3 deeper into the system and into the aquifer. This factor also explains why nitrate concentrations during low-discharge, groundwater recession periods, were higher in 1983 than 1982. As nitrate is displaced deeper in the soil-subsoil system, more nitrate would continue to be delivered to groundwater even as the water-table (potentiometric) surface lowered during recession. As the water-table surface lowers it is draining from lower subsoil horizons which generally contain less nitrate. This relationship also suggests that there was a relative balance in the amount of $\text{NO}_3\text{-N}$ available (among storage, displacement, and additions) in the soil-water system. Future deviations from this relationship may allow the determination of the impact of PIK landuse and chemical-use changes.

$\text{NO}_3\text{-N}$ Losses and Landuse

The time lag between changes in chemical land-treatment and changes in chemical quality in the groundwater (combined with the differences between crop-years and water-years) point out the problems in comparing the water-quality data from a given year with that year's landuse. However, during the period from about 1979 to 1983 landuse (and treatment) were relatively constant in

Table 12. Maximum measured concentrations for various, currently used, pesticides found in groundwater at Big Spring for WY-1982 and -1983.

Herbicides	WY-1982 μg/l	WY-1983 μg/l
Atrazine (atrazine)	2.5 (10.0)	5.1
Bladex (cyanazine)	0.70 (0.50)	1.2
Lasso (alachlor)	0.15 (6.00)	0.63
Dual (metolachlor)	--- (0.25)	0.62
Insecticides		
Dyfonate (fonofos)	---	0.11

(Data in parentheses form Dutton's Cave Spring.)

the Big Spring basin (particularly compared to the large changes related to PIK in 1983). Thus, some comparisons provide useful perspectives on the NO₃-N losses. Table 13 summarizes the NO₃-N losses for WY-1982 and 1983 in relation to landuse and land area in the basin.

As previously discussed, the NO₃-N discharged increased from an equivalent of 27 lbs-N/ac (31 kg-N/ha) to 43 lbs-N/ac (49 kg-N/ha). In the perspective of the acreage that has been in corn over the long-term (3-5 years in various rotations), the amount of N lost increased from 47 lbs-N/ac (52 kg-N/ha) in WY-1982 to 74 lbs-N/ac (83 kg-N/ha) in WY-1983. Table 13 also shows the N-losses in relation to 1982 and 1983 corn acreages. Again for perspective, the total NO₃-N losses in WY 1982 were equivalent to 33% of the applied fertilizer-N for 1982; the N-losses in WY-1983 were equivalent to 53% of 1982 applied chemical-N. The WY-1983 N-losses were equivalent to 83% of the chemical-N applied in the 1983-PIK year, but as noted, it is not reasonable to compare these figures.

The comparison of WY-1983 N-losses with the 1982 chemical-use data is reasonable, as discussed, because of the more constant antecedent landuse/chemical treatment and apparent relative balance in the groundwater-chemical system. Thus, it is fair to summarize that in northeast Iowa during a relatively wet year, such as WY-1983, an amount of N equivalent to about 50 % of the chemical fertilizer-N applied may be lost into groundwater-surfacewater supplies as NO₃ alone. This is a minimum figure, because it does not account for other forms of N that may be discharged with the water. These figures also do not consider other losses of fertilizer-N (or other available-N) from volatilization and perhaps denitrification. This figure of 50% while seemingly large is in good agreement with many other studies (as summarized in Libra et al., 1984; and as will be discussed in later sections of this report).

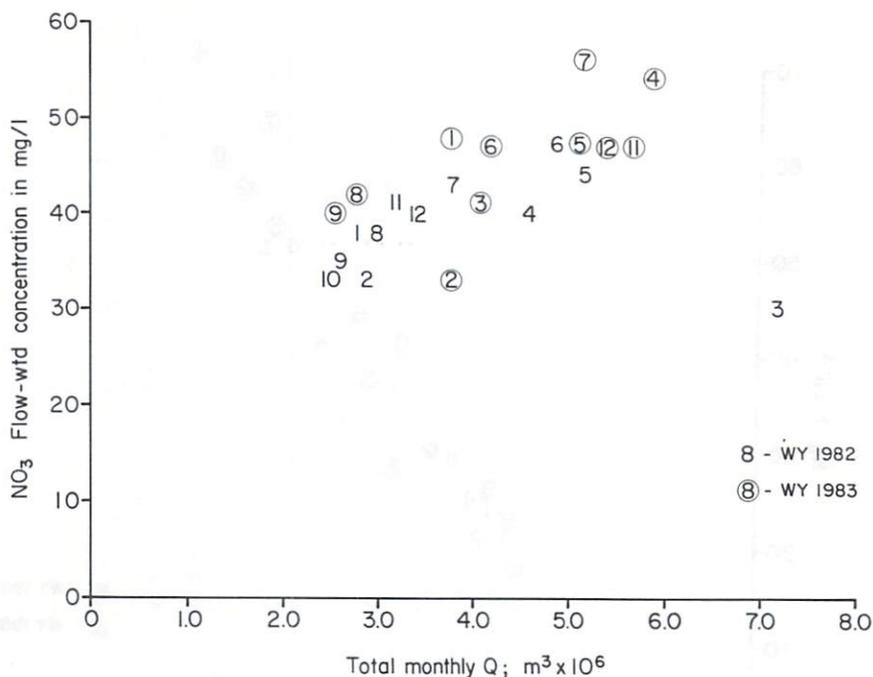


Figure 10. Total monthly water discharge at Big Spring vs. monthly flow-weighted, mean nitrate concentration at Big Spring .

MONITORING OF MAJOR DISCHARGE EVENTS

Two major and several minor runoff-discharge events were monitored in detail during the last year of study. The major runoff events included the main snowmelt period, 2/14/83-2/27/83, and the aftermath of a series of heavy rains, between 6/26/83-7/3/83. Data collected during these periods, and a discussion of the interpretation of this detailed data collection, are presented below.

Snowmelt Period Discharge Events -- 2/14/83-2/27/83

The snowmelt period is blocked out on figures 1 and 2, which show the discharge, climatic, and major chemical parameters monitored at Big Spring. Comparison of daily air temperature extremes and the discharge record indicates that minor melting and recharge began about 2/13/84, when daily maximum temperatures exceeded 40°F (4.4°C). Maximum temperatures above 50°F (10.0°C) on 2/19/83-2/20/83 caused major melting and recharge, with discharge exceeding 200 cfs (5.6 mcs) at Big Spring on 2/21/83. Minimum temperatures from 2/19/83-2/21/83 were essentially at 32°F (0°C), indicating that melting was probably continuous, although the rate of melting undoubtedly slowed

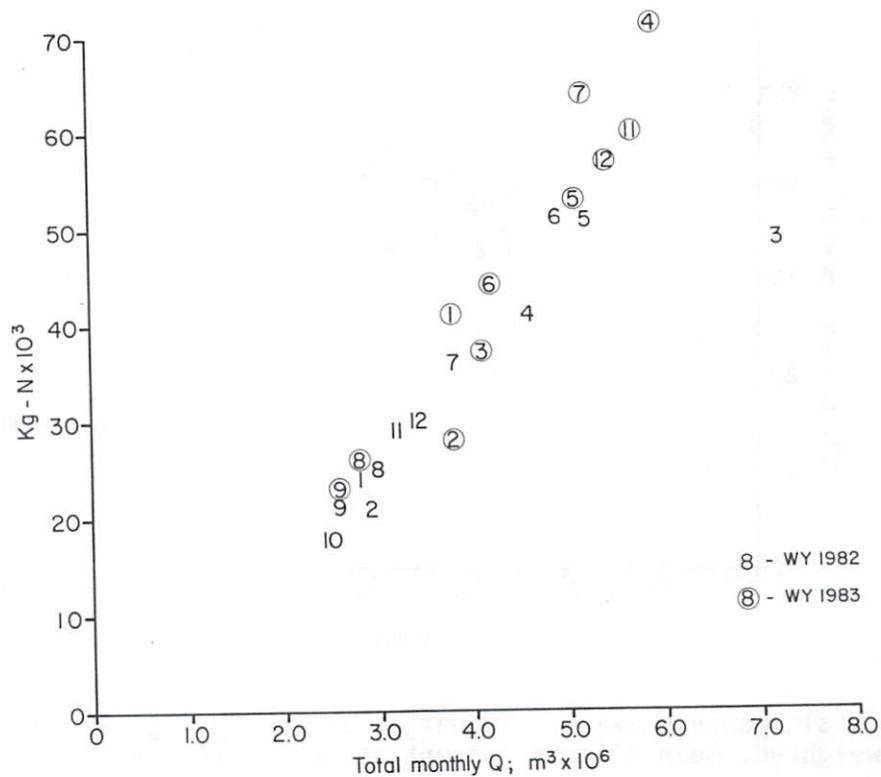


Figure 11. Total monthly water discharge at Big Spring, vs. total monthly nitrate discharge at Big Spring.

during the late evening and early morning hours. The effects of meltwater recharge on measured parameters is clearly shown on figures 1 and 2. Groundwater temperatures decrease from about 46°F (8°C) to about 40°F (5°C). Specific conductance decreases from 650 to less than 300 $\mu\text{mhos}/\text{cm}^2$, reflecting the low dissolved solids content of the meltwater and indicating limited interaction between the meltwater and the soil matrix and the aquifer. Nitrate concentrations decrease from about 40 mg/l to a low of 14 mg/l. Atrazine concentrations increase from the normal background level of 0.1-0.2 $\mu\text{g}/\text{l}$ to almost 1.0 $\mu\text{g}/\text{l}$.

Figure 12 is a detailed plot of discharge and nitrate concentrations for the snowmelt period. Peak discharge during the period 2/20/83-2/24/83 occur daily, roughly at midnight. These daily peaks in the hydrograph are likely related to changes in the rate of melting, which result from diurnal temperature variations. Major melting probably began to occur daily at 0900 to 1100 hours. As meltwater forms and becomes recharge, the potentiometric surface below recharge areas rises and groundwater flow rates increase. Discharge at Big Spring begins to rise, in response to the rising potentiometric surface below recharge zones, at 1200-1400 hours, peaking roughly at midnight. As much of the soil was still frozen during this period and the discharge at Big

Table 13. Summary of nitrate-N loss from the Big Spring basin in relation to landuse for 1982-1983 water years.

Total NO₃-N discharged from basin in lbs-N/acre (kg-N/ha) equivalent.

	1982*	1983
lbs-N/acre of basin (kg-N/ha)	27 (31)	43 (49)
lbs-N/acre of long-term row crop (land in corn rotation) (kg-N/ha)	47 (52)	74 (83)
lbs-N/acre corn - 1982 acreage (kg-N/ha)	58 (65)	93 (104)
lbs-N/acre corn - 1983 (PIK) acreage (kg-N/ha)		123 (138)
% of applied chemical-N, 1982	33%	53%
% of applied chemical-N, 1983 (PIK)		82%

* Data from Hallberg et al., 1983.

Spring is highly diluted, much of this recharge must have been occurring as runoff to sinkholes, and as macropore flow (directly or indirectly). The time of travel from major sinkhole areas to Big Spring, measured during dye traces, is at least 18 hours (Heitman, 1972; Hallberg et al., 1983; also see discussion of 6/26/83-7/22/83 period, this report).

The very short time interval between the onset of major melting and the beginning of daily discharge increases suggests that substantial portions of the conduit-flow system are inundated under high discharge conditions (minimum discharge preceeding a diurnal discharge peak for the period 2/20/83-2/24/83 was 85 cfs, or 2.4 cms). The recharge effects during this snowmelt period must be transferred as a pressure wave through the system, because the increase in discharge takes place almost immediately. Note that the pressure effects are not completely efficient, as the offset between peak melting and peak discharge is about 9 hours (assuming that peak melting occurs daily at about 1500 hours).

Discharge peaks were not accompanied by the lowest nitrate concentrations, rather they arrive 12-14 hours later (figure 12). This offset, or lag-time between discharge peaks and lowest nitrate levels occurs because the water with-

in the conduits, prior to major daily melting, must be flushed out, or displaced, before the new daily recharge water actually reaches the spring. This is analogous to the displacement water noted by Hallberg and others (1983) for the Big Spring flow system. Again, noting that peak discharge occurs at midnight, with lowest nitrate levels 12-14 hours later, groundwater travel times from sinkhole basins to Big Spring of 21-23 hours are indicated, similar to the high discharge condition travel time noted during dye traces and other discharge events.

The preceding discussion is largely limited to the hydrologic and chemical effects of meltwater recharging the conduit-flow parts of the Galena aquifer via sinkholes. The rapid hydrograph responses and chemical characteristics of discharge water indicate this is the dominant process occurring, during much of the period. Infiltration will be limited until the soil zone thaws and allows more complete downward percolation of meltwater. Initially, infiltration must be confined to flow along macropores, particularly frost fractures and other zones of secondary permeability. The response time of the macropore zones to recharge would likely be slower than that associated with runoff recharge and conduit flow, but considerably faster than that of infiltration-displacement flow through the soil matrix.

The frozen matrix of the soil, where the bulk of the soluble chemicals are in storage, remains largely isolated from this macropore flow, and thus, chemically the macropore-water resembles snowmelt-runoff water and is dilute in nitrate. This is shown by the change in nitrate concentrations in the tile-drainage water (figure 6, Appendix 1). The tile-line waters are a representation of the shallow-infiltrating groundwater, moving through the soil profile. During snowmelt the water discharge from the tile lines increased but nitrate concentrations dropped sharply by 30-70% (in both 1982 and 1983 monitoring, see Hallberg et al., 1983). Yet as melting continues, and the soil matrix thaws, nitrate concentrations rise back to the level they were at prior to snowmelt. If this initial infiltration water, recharging the tile drainage, were true displacement flow the nitrate concentrations would not abruptly decrease and then rise again to their prior levels. As the soil thaws the infiltration water begins to interact with increasing amounts of the soil matrix, and thus it will begin to displace the matrix-held chemicals, such as nitrates, with the infiltration water. The point in time where chemicals, such as nitrate, and various infiltration mechanisms begin to function, and the rate at which the volume of water (and chemicals) transported by these mechanisms increases is unclear, and probably varies areally across the basin.

The increase in atrazine concentration, concurrently with the decrease in nitrate at Big Spring is somewhat anomalous. The high concentrations of soluble pesticides that occur in runoff-runin recharge water generally come from the interaction of the surfacewater with the soil; from contact with the soil surface and soil-particles during sheetwash, and by very shallow lateral macropore flow (or interflow) down the hillslope. As discussed, this interaction could not take place during the early snowmelt period, because the soil was frozen and generally covered with snow. Yet, atrazine concentrations in groundwater at Big Spring rose to the second-highest level recorded in the monitoring to that date (0.88 µg/l).

The high snowmelt discharges at Big Spring were marked by high suspended

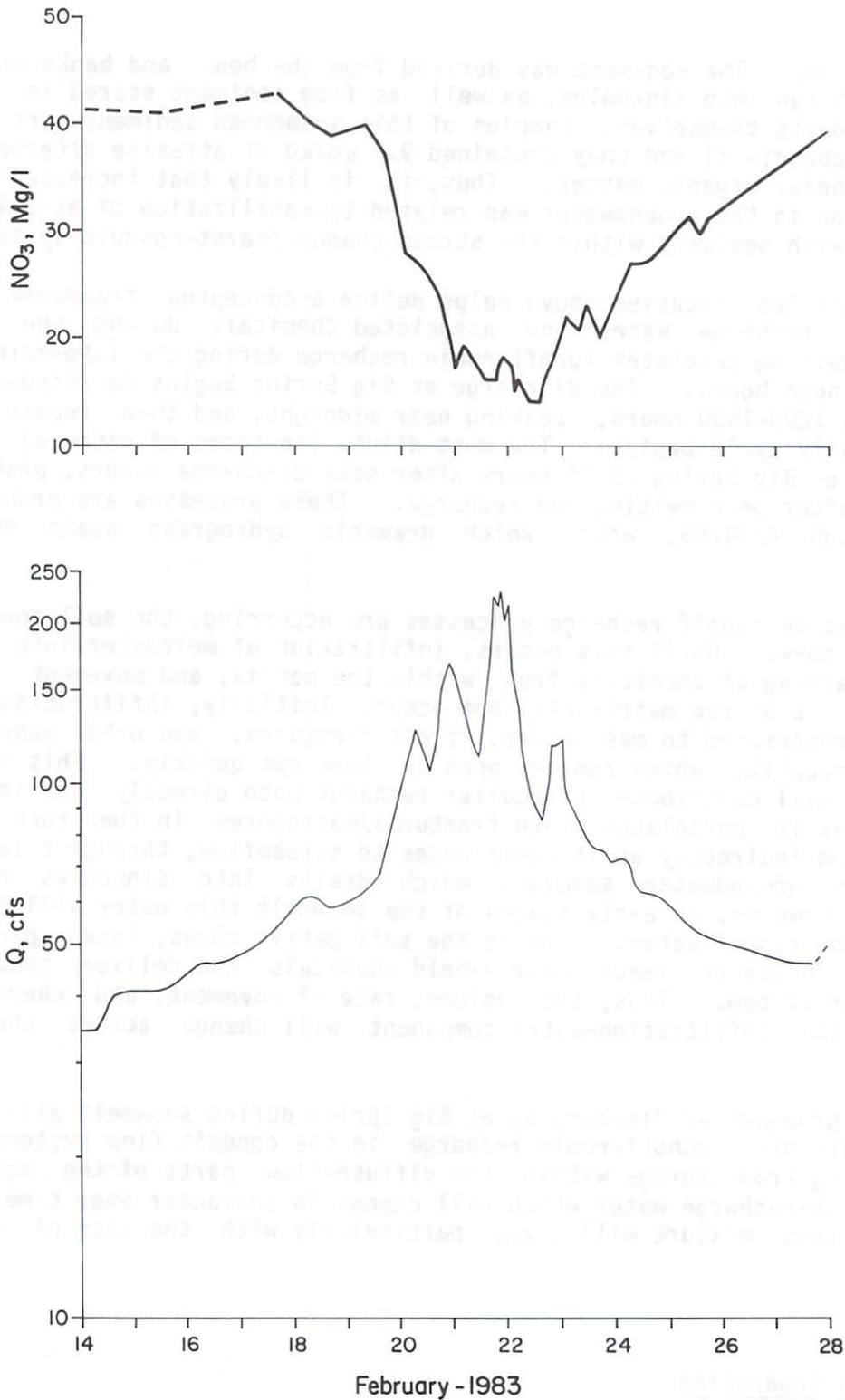


Figure 12. Groundwater discharge and nitrate concentration at Big Spring during February, 1983, snowmelt event.

sediment loads. The sediment was derived from the beds and banks of surface streams that run into sinkholes, as well as from sediment stored in the sub-surface conduits themselves. Samples of this suspended sediment were analyzed (Table 9, Appendix 1) and they contained 9.2 µg/kg of atrazine attached to the sediment and/or organic matter. Thus, it is likely that increased atrazine concentration in the groundwater was related to mobilization of atrazine which was stored with sediment within the stream channel/karst-conduit system.

The relationships discussed above helps define a conceptual framework for the delivery of recharge water and associated chemicals during the snowmelt period. Melting generates runoff-runin recharge during the late-morning and early-afternoon hours. The discharge at Big Spring begins to respond to this recharge at 1200-1400 hours, peaking near midnight, and then recessing until the next daily cycle begins. The most dilute (in terms of nitrate) recharge water reaches Big Spring 12-14 hours after peak discharge occurs, probably 20-24 hours after peak melting and recharge. These processes are probably dominant through 2/24/83, after which dramatic hydrograph peaks no longer occur.

While the above runoff recharge processes are occurring, the soil zone is beginning to thaw. Until this occurs, infiltration of meltwater into the soil matrix, leaching of chemicals from within the matrix, and movement of frozen soil water out of the matrix will not occur. Initially, infiltration recharge is likely restricted to macropores, frost fractures, and other zones of enhanced permeability which remain open or thaw out quickly. This macropore-flow water will contribute to aquifer recharge both directly and indirectly: directly as it percolates into fractures/macropores in the rocks of the aquifer; and indirectly as it contributes to streamflow, through tile-drainage and shallow groundwater seepage, which drains into sinkholes or losing reaches. However, in early stages of the snowmelt this water will chemically resemble the runoff water. Then as the soil matrix thaws, less rapidly moving water will begin to leach matrix-held chemicals and deliver them to the groundwater system. Thus, the volume, rate of movement, and chemical character of the infiltration-water component will change across the snowmelt period.

Thus, the groundwater discharging at Big Spring during snowmelt will be a complex mixture of: runoff-runin recharge in the conduit flow system; groundwater coming from storage within the diffuse-flow parts of the aquifer; and infiltration-recharge water which will change in character over time. Proportions of this mixture will vary, particularly with the rate of runoff recharge.

Hydrograph Separation

Separation of the snowmelt-period hydrograph into infiltration recharge diffuse-flow and runin-recharge, conduit flow components was attempted using the methods described by Hallberg and others (1983): an analytical method and a method based on measured physical or chemical parameters. The separations are complicated by a number of factors. First, the large daily variations in discharge give the hydrograph a complex multi-peaked form. Second, while

periods of major melting and surface runoff/runin recharge are readily identified by the hydrograph response, some melting and runoff occurred virtually throughout the period; no single, defined period of runoff exists. Third, uncertainties exist as to the importance and mechanism (macropore vs. matrix flow) of infiltration recharge across the period. The analytical separation of the hydrograph assumes infiltration occurs without the presence of a slowly disappearing flow barrier such as the frost zone. Fourth, chemical separations are hampered by the number of flow components that may be present, each with differing chemical characteristics: true meltwater runoff; groundwater stored within the diffuse-flow parts of the aquifer; macropore-flow water, and matrix-infiltration water. Separation of any discharge hydrograph into only two components of flow is an oversimplification of a complex series of processes. However, when the separations are considered in light of the conceptual framework of hydrology and chemical delivery described in the previous section, they provide insights into the nature of those complex processes, and therefore a better understanding of the system.

Analytical separation of the hydrograph from this period (figure 13) indicates that of the 2025 acre-feet (2.50 million m³) of water discharged about 1300 ac-ft (1.60 million m³), or 64%, was supplied by diffuse flow. If sufficient data were available on the concentrations of constituents (pesticides, organic-N, ammonium-N, etc.) mobilized in the runoff water, the analytical separation could be checked for consistency (see section on separation of 6/26/83-7/22/83 hydrograph, for example). As detailed data were not available, the results of the analytical separation for this complex event are somewhat speculative, but are presented here for comparative reasons.

Nitrate concentrations were monitored in some detail at Big Spring (figure 12) during this period and these data were also used to separate the hydrograph (see figure 14). A two component mixing model was used. Required data include: 1) total groundwater discharge at Big Spring; 2) measured nitrate concentration at Big Spring; and 3) estimated nitrate concentrations in each component. Initial estimates were: 40 mg/l nitrate in the diffuse-flow component, based on measured concentrations during groundwater base-flow at Big Spring, before and after the snowmelt period; and 10 mg/l nitrate in the surface runoff recharge component, based on measured surfacewater concentrations of 7-14 mg/l during the period. Results of this separation are shown on figure 14. The problems with the separation are readily apparent. The diffuse-flow hydrograph indicates changes in diffuse flow that are almost as rapid as the total hydrograph variations, an unrealistic conclusion. Diffuse-flow contributions are also forced to drop dramatically, almost to 10 cfs (0.28 cms). These problems are largely the result of the interplay of the large daily discharge variations which occur, and the 12-14 hour offset between the peak discharge and the later arrival of dilute recharge water. This results in low nitrate concentration during low discharge periods and high nitrate concentrations during the major runoff-conduit flow periods; the opposite of how the system responds (Hallberg et al., 1983).

The observed 12-14 hour lag-time between peak discharge and the associated lowest nitrate level was used to construct a more realistic nitrate-based separation. The measured nitrate values were offset about 12-14 hours, so that the dilute nitrate values coincide with the peak discharges. The same two-component mixture was assumed, however, nitrate concentrations in

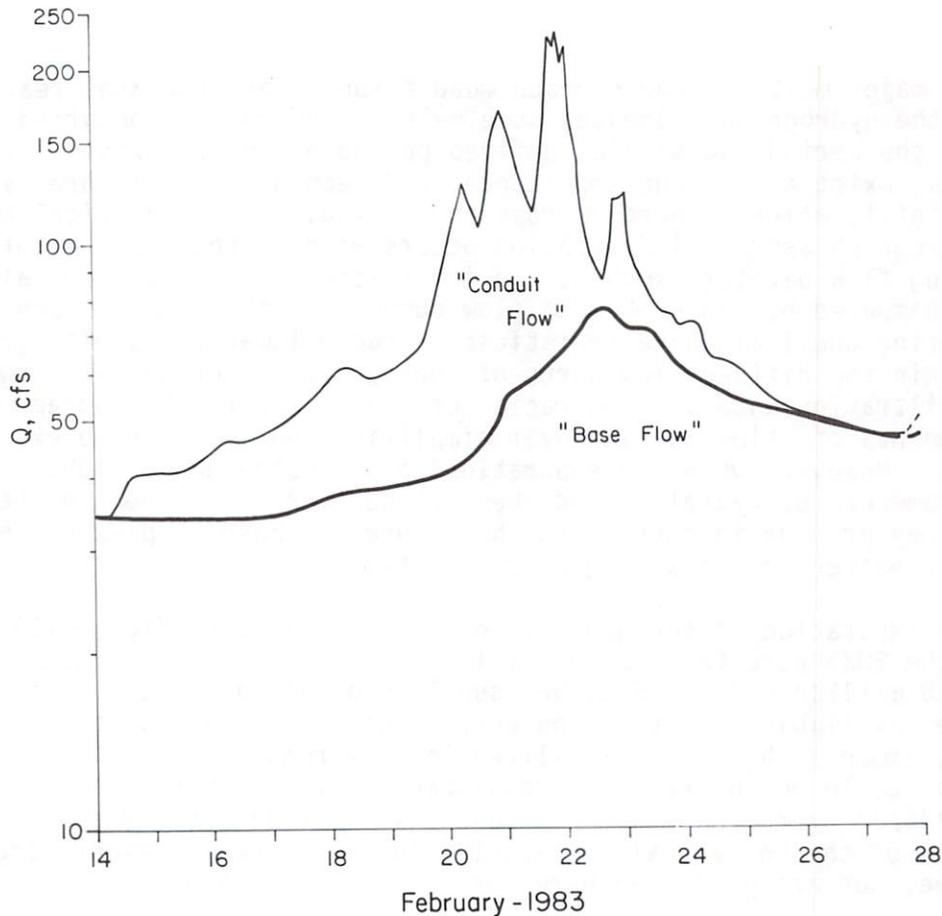


Figure 13. Analytical hydrograph separation of February, 1983, snowmelt event.

the runoff-recharge component were estimated to be 5 mg/l instead of 10 mg/l, which is more representative of the smaller surfacewater sites which drain into sinkholes. Figure 15 shows the resulting hydrograph. Comparison with figure 14 indicates that the major, anomalous peaks in the diffuse-flow hydrograph are largely smoothed out. The irregular form of the diffuse-flow hydrograph, even with these modifications, probably results from varying flow rates, and therefore travel times, from various parts of the basin to Big Spring. Other subcomponents of flow, such as described by Hallberg and others (1983), also may contribute to these irregularities. A smoothed curve (dashed-line, figure 15) fitted to this separation indicates a baseflow volume of about 1,330 acre feet, 66% of the total discharge. This is in close agreement with the diffuse-flow value generated by the analytical separation. However, a comparison of the structure of the two separations (figures 13 and 15) shows that major differences exist. The analytical separation indicates that runoff-recharge occurs during the period 2/14/83-2/19/83, and suggests a generally high diffuse-flow component for the period 2/19-2/27 (relative to the nitrate based separation). The nitrate-based separation indicates that all of

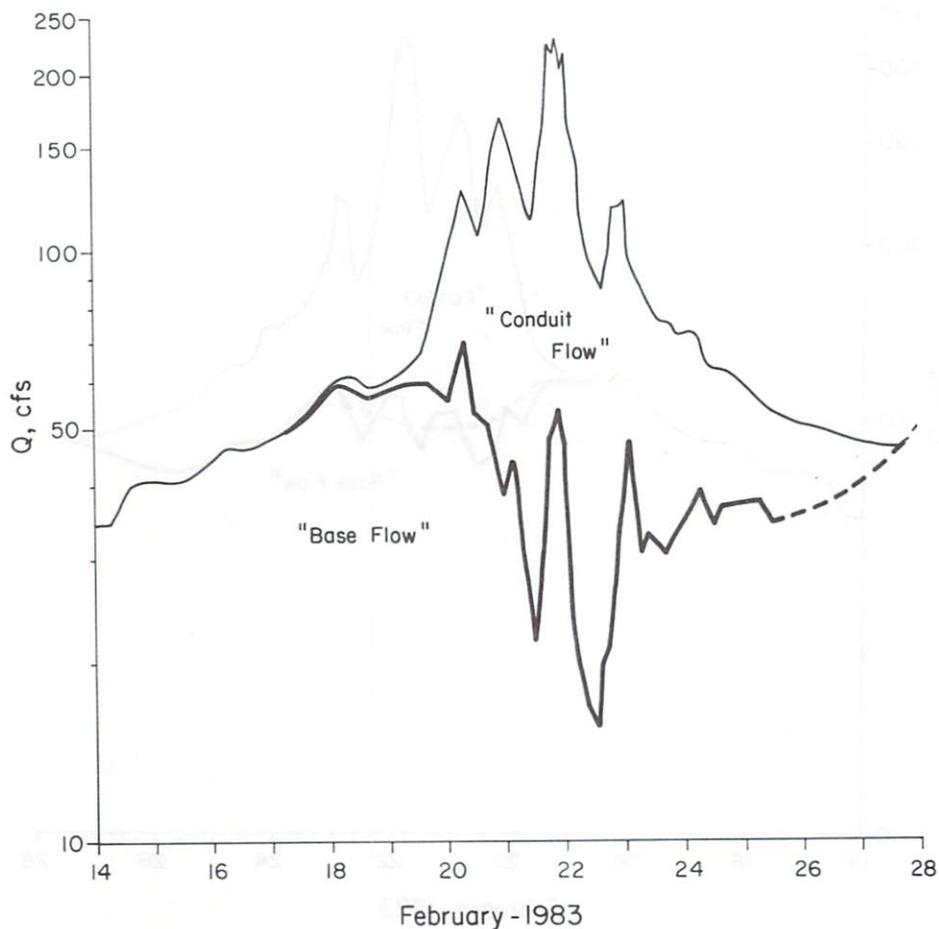


Figure 14. Nitrate (chemical)-based hydrograph separation for February, 1983, snowmelt event.

the discharge from 2/14-2/19 is diffuse flow, because nitrate levels do not fall below 40 mg/l. The lower diffuse-flow component indicated for the period 2/14-2/27 is the result of the low nitrate concentrations (figure 12). During the 2/19/83-2/27/83 period, the nitrate-based separation indicate that 55% of discharge is baseflow; the analytical separation 60%.

Several features of the nitrate data and the nitrate-based separation warrant comment. First, is the failure of nitrate levels to respond significantly during 2/14/83-2/19/83, as runoff-recharge slowly increases discharge from about 35 to 60 cfs (1.0-1.7 cms). Conceptually, nitrate concentration should have shown some decrease across this period. An examination of the nitrate record indicates that nitrate levels do begin to drop on 2/18/83; however, they only drop from 43 mg/l to 40 mg/l, and therefore the nitrate-based separation does not reflect this drop. Also, under relatively low discharge conditions (less than 50 cfs; 1.4 cms), flow rates within the conduit system are considerably lower than under high flow conditions (>100 cfs; 2.9 cms). Travel times from sinkhole basins to the spring under the discharge conditions

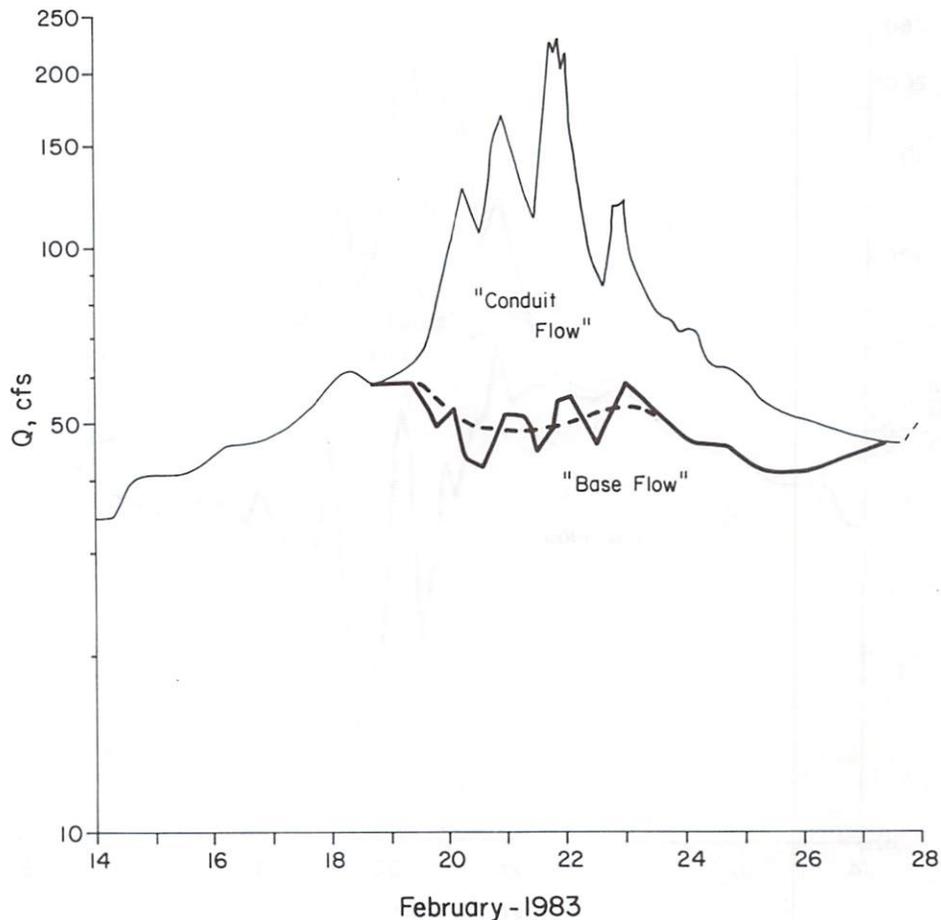


Figure 15. "Offset" nitrate (chemical)-based hydrograph separation for February, 1983, snowmelt event.

existing during this period are likely on the order of at least 48-72 hours (see Hallberg et al., 1983). Several days would be needed before meltwater reached the spring and caused any change in nitrate levels. Diffuse-flow discharge, as derived by nitrate concentrations, rises from 35 to about 50 cfs from 2/14/83-2/18/83, but does not increase above 55 cfs (1.6 cms) after that even as total discharge exceeds 220 cfs, suggesting that under peak-discharge conditions almost 75% of the discharge is surface runoff.

This percentage is high, and uncertainties in the processes delivering water and chemicals precludes a final judgement. Actual diffuse flow-infiltration recharge may be greater, but if so, it must contain less than 40 mg/l nitrate. If macropore flow is contributing significant volumes of relatively low-nitrate water, a separation similar to that shown in figure 13 would result. This explanation requires that little matrix-flow, high nitrate soil water is being discharged from Big Spring until the end of 2/14/83-2/27/83 period. The volume of water lying above the diffuse-flow hydrograph (figure 13) could then simply be considered as "snowmelt-event" water, which was delivered into the

aquifer by runoff to sinkholes and macropore-flow contributions. Direct macropore contributions that reach the spring within the 2/14/83-2/27/83 period probably occur in shallow bedrock areas near the major conduit zones. In these areas, macropores are more likely to be in more direct connection with the aquifer and flow rates in the underlying aquifer are greatest. It is likely that most of the chemical effects that are ascribed to infiltration processes soon after a recharge event in Big Spring discharge are related to water that infiltrate in, and adjacent, to the sinkhole basin areas, where extensive areas of shallow bedrock (with vertical and horizontal solution conduits) occur.

The volume of "snowmelt-event" waters for the period 2/19-2/27 is about 700 acre-feet (0.86 million m³) based on the nitrate separation. During the period 2/14/83-2/18/83, before nitrate levels fall below 40 mg/l (figure 12), the analytical separation suggests that an additional 120 acre-feet (0.15 million m³) of snowmelt was discharged. If the total volume of snowmelt water, 820 acre-ft (1.01 million m³), is spread over the sinkhole basins (11.5 mi²; 29.8 km²), this represents 1.34 inches (34 mm) of recharge. Data on the depth and moisture content of the accumulated snowfall within the basins are not available. Data from the surrounding weather stations indicates that snow depths were 8-12 inches prior to melting. Snowfall during January and February in Elkader contained 1.68 inches (42.7 mm) of moisture, about 0.34 inches (8.6 mm) more than the nitrate-based separation indicated was delivered to Big Spring. Some meltwater undoubtedly remained in slow transit within the soil zone, and some snow also probably remained after 2/27/83. This simple comparison indicates that the nitrate-based separation, and the concept of a macropore flow component in the "event" water, are at least a realistic approximation of the water and chemical yield for the snowmelt event. A better quantification of the separation methods is possible from the June-July events discussed in later sections of the report.

April 1983, Discharge Events

During April 1983, gentle rains and snowmelt generated some unique discharge and water-quality events at Big Spring (see figures 1 and 2). A detailed hydrograph and plot of the nitrate concentrations at Big Spring are shown on figure 16. From March 27 to 30 about 0.25 inches (6.4 mm) of precipitation fell as snow which gradually melted and infiltrated the soil. On April 1 and 2 about 0.8 inches (20.3 mm) of rain fell overnight. April 2-3 about 0.4 inches (10.2 mm) of rain fell and then again overnight on April 5 and 6 another 0.2 inches (5.1 mm) of rain fell. Little runoff was generated.

The discharge at Big Spring rose, over a 48 hour period from approximately 51 cfs (1.45 cms), on 4/1/83, to about 83.5 cfs (2.37) on 4/3/83. By 4/5/83 discharge had risen to about 85 cfs (2.40 cms). While this is a sharp rise, it is less steep than the increases in discharge associated with major runoff-conduit flow events. The discharge remained stable at this level (figure 16) for 3 days, then began to drop. By 4/9 discharge had declined to about 77 cfs (2.18 cms).

Overnight April 8-9, 0.34 inches (8.6 mm) of precipitation fell as snow, and

began to melt. This was followed by 0.37 inches (9.4 mm) of rain on 4/9-10. The same weather patterns continued and more rain fell on 4/12-13 and 4/13-14, totalling 0.19 inches (4.5 mm) and 0.43 inches (10.9 mm), respectively, and again on 4/15 and 4/17, about 0.04 inches (1.0 mm) each day. A little runoff was generated on 4/10 and 4/14.

With these added inputs the discharge at Big Spring gradually rose again (figure 16), beginning on 4/9 and 10, rising from 77 cfs (2.1 cms) to about 87 cfs (2.4 cms) on 4/13, and then rising somewhat more steeply to its maximum of about 100 cfs (2.83 cms) on 4/14 (1530 hours). Discharge then fluctuated, but gradually receded to about 65 cfs (1.84 cms) on 4/29/83.

Field observations noted that little runoff was generated by these precipitation events. The gradual rise and recession, and the initial flat-topped discharge-hydrograph (figure 16) all imply that these rises in discharge were principally related to infiltration recharge. Some minor pulses of runoff water are likely involved with the initial rise and with the few sharper discharge "peaks" on 4/14 through 4/18. The flat-portion of the hydrograph suggests simply that a new, stable base-flow discharge had been attained, and was being sustained, by this infiltration. As discussed for the snowmelt event, the response to this infiltration is still relatively rapid (for groundwater systems), which suggests that this infiltration-discharge increase is, at least, initiated in the sinkhole basins, and other shallow-bedrock areas where: 1) infiltration can take place directly and rapidly; and 2) where this infiltration recharge can be rapidly conducted, in large part through the conduit-flow system, to Big Spring.

As would be expected for an event generated by infiltration recharge, nitrate concentrations increased in the groundwater at Big Spring. The most unique aspect of this event is the nature of the nitrate concentration changes (figure 16). Prior to the precipitation-discharge events nitrate concentrations were relatively constant at about 43 mg/l. On the discharge rise of 4/3 nitrate decreased to 41 mg/l. Then, within 24 hours, between 4/4 and 4/5 nitrate concentrations rose sharply to 51 mg/l. This rise occurs about 48 hours after the discharge rise. Nitrate concentrations remained at this level for four days. Two days after discharge had begun to decline nitrate began to decrease slightly. By this time discharge was at the low-level of 4/9. As the discharge began to gradually rise again on 4/9-10, nitrate continued to decline to 49 mg/l on 4/10 and then values fluctuated until 4/12. Then, from the morning of 4/12 to the morning of 4/13, while discharge was still on a gradual rise, nitrate concentrations rose sharply, from 49 to 72 mg/l (figure 16). Nitrate concentrations remained high, fluctuating between 69 and 75 mg/l for 5 days, until 4/18. During this time the discharge rose, reached its peak value, then fluctuated and began to gradually decline. During this discharge recession, between the mornings of 4/18 and 4/19 nitrate concentrations fell as dramatically as they had risen, dropping from 75 mg/l to 51 mg/l in about 24 hours. Nitrate then gradually declined to 46 mg/l by 4/26.

Such changes in nitrate concentration had not been observed before at Big Spring. For purposes of discussion we have termed these phenomenon nitrate "plateaus," from the overall shape of the plot of concentration with time. As shown on figure 16, these plateaus are marked by a sharp rising limb, a relatively flat-topped stable portion, and a sharp termination. These plateaus mark a unique phenomenon which must be related to the overall

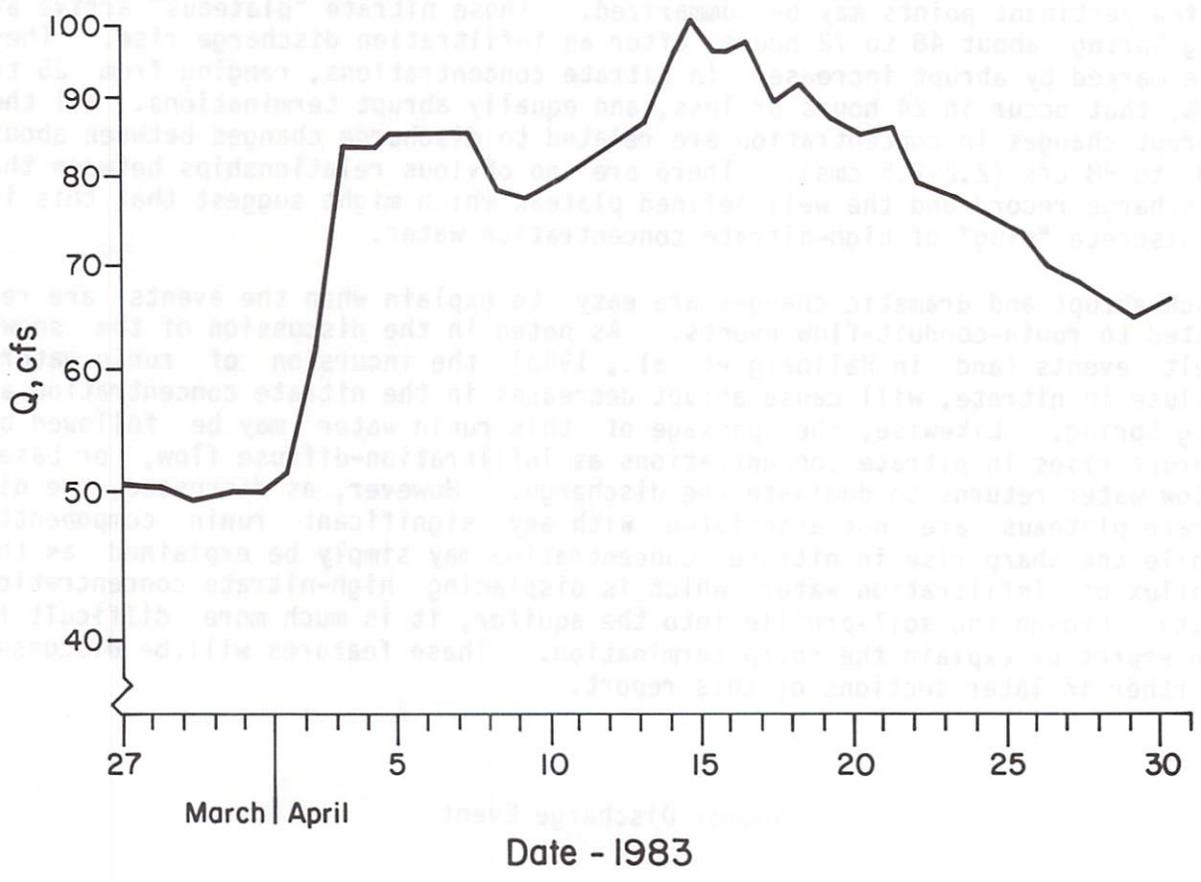
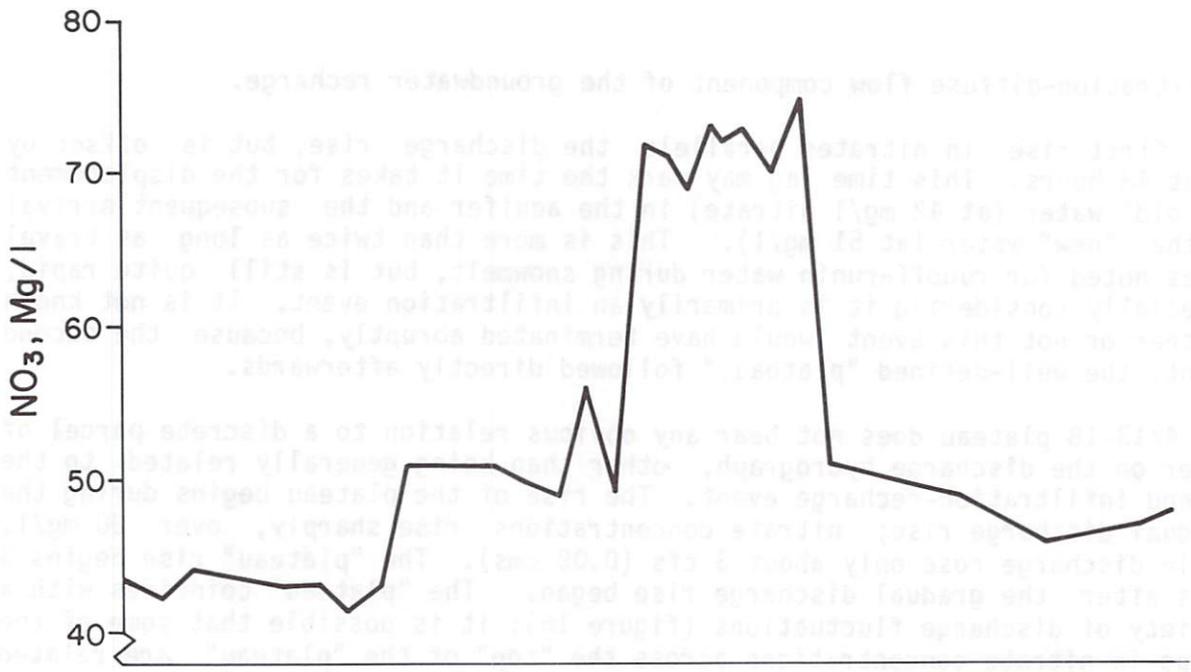


Figure 16. Groundwater discharge and nitrate concentrations at Big Spring during spring, 1983, events.

infiltration-diffuse flow component of the groundwater recharge.

The first rise in nitrates parallels the discharge rise, but is offset by about 48 hours. This time lag may mark the time it takes for the displacement of "old" water (at 42 mg/l nitrate) in the aquifer and the subsequent arrival of the "new" water (at 51 mg/l). This is more than twice as long as travel times noted for runoff-runin water during snowmelt, but is still quite rapid, especially considering it is primarily an infiltration event. It is not known whether or not this event would have terminated abruptly, because the second event, the well-defined "plateau," followed directly afterwards.

The 4/13-18 plateau does not bear any obvious relation to a discrete parcel of water on the discharge hydrograph, other than being generally related to the second infiltration-recharge event. The rise of the plateau begins during the gradual discharge rise; nitrate concentrations rise sharply, over 20 mg/l, while discharge rose only about 3 cfs (0.08 cms). The "plateau" rise begins 3 days after the gradual discharge rise began. The "plateau" coincides with a variety of discharge fluctuations (figure 16); it is possible that some of the drops in nitrate concentrations across the "top" of the "plateau" are related to minor pulses of runin-conduit flow water on 4/10 and 4/14. The abrupt termination of the "plateau" simply occurs during gradual recession.

A few pertinent points may be summarized. These nitrate "plateaus" arrive at Big Spring about 48 to 72 hours after an infiltration discharge rise. They are marked by abrupt increases in nitrate concentrations, ranging from 25 to 50%, that occur in 24 hours or less, and equally abrupt terminations. All the abrupt changes in concentration are related to discharge changes between about 78 to 88 cfs (2.2-2.5 cms). There are no obvious relationships between the discharge record and the well-defined plateau which might suggest that this is a discrete "slug" of high-nitrate concentration water.

Such abrupt and dramatic changes are easy to explain when the events are related to runin-conduit-flow events. As noted in the discussion of the snowmelt events (and in Hallberg et al., 1983) the incursion of runin water, dilute in nitrate, will cause abrupt decreases in the nitrate concentration at Big Spring. Likewise, the passage of this runin water may be followed by abrupt rises in nitrate concentrations as infiltration-diffuse flow, or base-flow water returns to dominate the discharge. However, as discussed, the nitrate plateaus are not associated with any significant runin components. While the sharp rise in nitrate concentration may simply be explained as the influx of infiltration water which is displacing high-nitrate concentration water through the soil-profile into the aquifer, it is much more difficult to interpret or explain the sharp termination. These features will be discussed further in later sections of this report.

Summer Discharge Event

During late June and early July, 1983, a series of rainfall events generated a major runoff event in the Big Spring basin (see figures 1 and 17). Between 6/26 and 7/3 about 11 inches (280 mm) of rain fell in the basin. This produced a peak discharge at the Big Spring of about 220 cfs (6.2 cms) at 1400

hours (2 p.m.) on 7/1/83. A variety of detailed water-quality data were collected to document the nature of this major runoff-runin event in the Big Spring karst basin. The following sections will outline the details of these events and observations (between 6/26/83 and 7/25/83).

Antecedant Conditions and Precipitation

Preceding these events the weather had been warm and dry in the basin. Consequently, the groundwater discharge from Big Spring had been in a gradual recession since flow events in late May. The discharge had declined to about 45 cfs (1.3 cms) at the Big Spring, equivalent to about 51 cfs (1.4 cms) for the basin (i.e., including Back Spring, etc., see Hallberg et al., 1983 for details).

Heavy, intermittent showers began in the basin during the afternoon of 6/26, and continued into late morning of 6/27. About 3.25 inches (82.6 mm) of rain fell between 1400 hours on 6/26, and continued into late morning of 6/27. About 3.25 inches (82.6) of rain fell between 1400 hours on 6/26, and 0700 hours 6/27 (figure 17). Another 1.2 inches (30.5 mm) fell between 0700 and about 1100 hours on 6/27. (IGS staff could not get into the area until later in the day of 6/27, so there is not as detailed a record of these early events, as there is for the later events.)

Even with nearly 4.5 inches (114 mm) of rain, little runoff was generated because of the dry antecedant conditions. As noted in prior work in the basin, this area is marked by high rates of infiltration (see Hallberg et al., 1983).

Intermittent rain continued. On 6/28 a few scattered showers dropped 0.15 inches (3.8 mm) of precipitation in the basin. On 6/29, 0.65 inches (16.5 mm) of rain fell between 0500 and 0700. This rain generated some runoff and about 0900 hours dye was injected in the water running into two sinkholes on the east and west sides of the basin. Later on 6/29, between 1700 and 2000 hours 2.5 inches (62.5 mm) of additional rain fell (figure 17). This heavy rain, following the 5.25 inches (133.4 mm) which had fallen in the preceding three days, generated substantial runoff and flash floods in some small sub-basins in the Big Spring basin, with peak runoff occurring about 1900 hours.

No rain fell on 6/30 until light rain began about 2350 hours. This rain continued until 0330 on 7/1, and totalled about 0.45 inches (11.4 mm). Later on 7/1, from 0550 to 0820 hours another 1.2 inches (30.5 mm) of rain fell. Additional lighter rains continued on 7/2 and 7/3: on 7/2, 0.17 inches (17.8 mm) fell between 0500 and 0800, 0.2 inches (5.1 mm) between 0930-1050, 0.6 inches (15.2 mm) between 1200 and 1400 hours; on 7/3, 0.3 inches (7.6 mm) between 1915 and 2030 hours. No more rain fell in the basin for over 2 weeks. A few light rains occurred between 7/18 and 7/25.

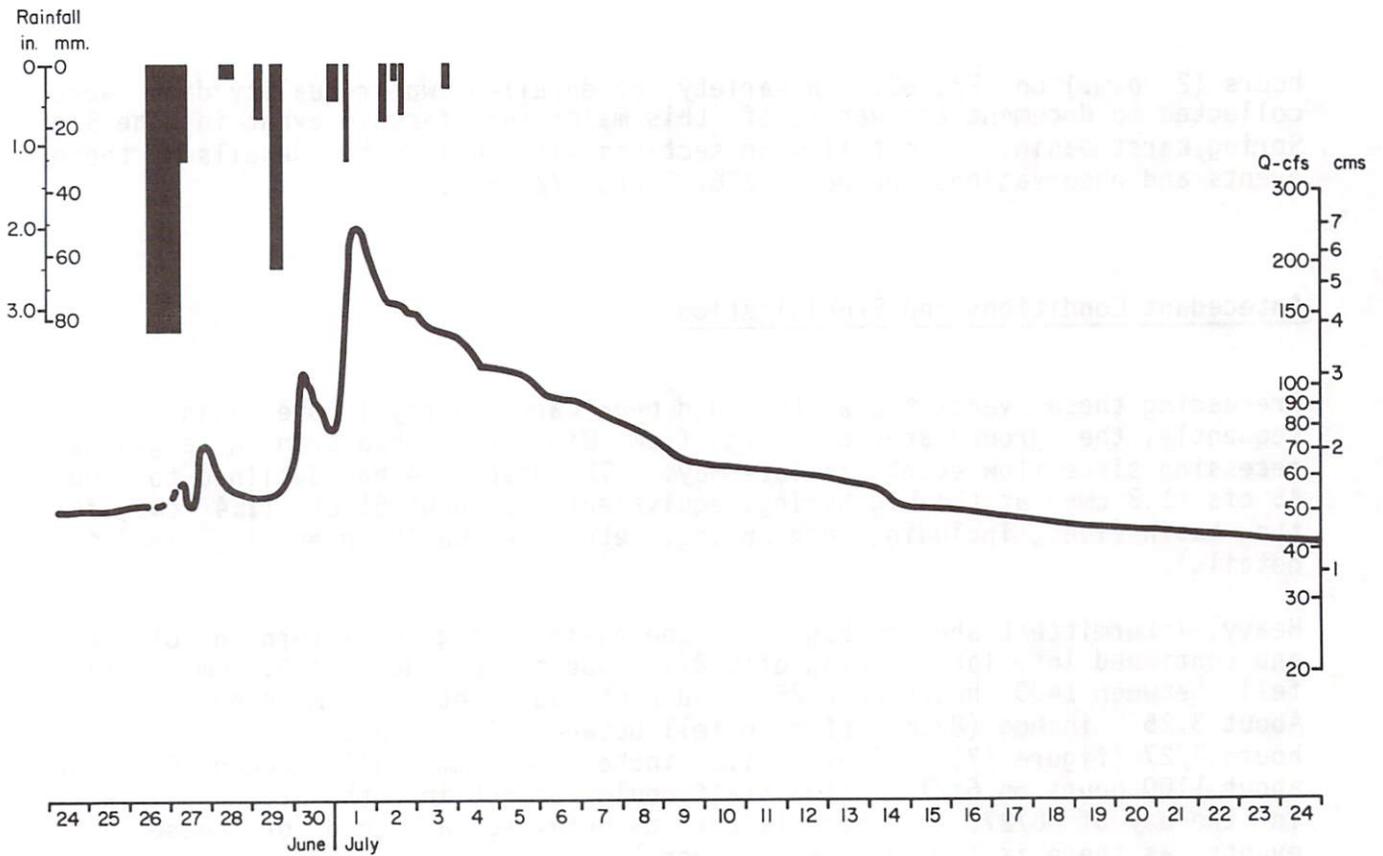


Figure 17. Groundwater discharge and precipitation data for Big Spring during mid-summer discharge event.

Surfacewater Discharge and Water Quality

Intermittently during these events water quality samples were collected from a number of surfacewater and tile line sites. Stream discharges were also measured at the stations in the Bugenhagen basin (figure 4). Pertinent data from the downstream (Boog-D) station will be summarized here (figure 18 and 19) and all the data are given in the Appendix. The Boog-D station is a short distance upstream from where this stream discharges into a series of sinkholes.

Little runoff was generated by the first few rainfall events. The discharge at Boog-D on 6/27 (2030 hrs.) and 6/28 (1500 hrs.) was about 1 cfs (28.3 l/s). There was no field evidence of any substantial discharge (e.g., greater than about 5 cfs; 140 l/s), and the very small hydrograph peaks at Big Springs on 6/27 (see figure 17 and 1) also suggest very little runoff ("runin" to sinkholes). On 6/29 some runoff occurred with the early morning rain (0500-0700 hours). By 0900 the stream had already receded to about 3.5 cfs (99 l/s), when dye was injected into the stream water running into the sinkhole. The

heavy rains on the evening of 6/29 (1700-2000 hrs.) generated a flash flood in the basin, and the stream rose and overflowed its banks in a very short time with peak discharge at 1900 hours which could not be gaged but was estimated at about 25 cfs (710 l/s). The sinkholes could not take all of this water and the stream overflowed the sinkhole area and spewed water out over the alluvial plain of the Silver Creek. This water infiltrated into the alluvial-plain sediments. This peak runoff-runin event generated the large hydrograph peak of 7/1 at Big Spring. The stream recessed overnight and by 0700 on 6/30 the discharge was 3.4 cfs (96 l/s). However, no runoff, (e.g., sheet or rill flow) was actually occurring at this time. All this discharge was shallow groundwater flow; interflow, tile drainage, and/or bank-storage return flow. The early morning rains on 7/1 again generated actual runoff, with a discharge of about 8 cfs (227 l/s; figure 18). After this time, stream discharge slowly recessed, as base-flow remained relatively high. By 7/8 discharge was still at 2.6 cfs (74 l/s), but by 7/28 it was only 0.3 cfs (9.6 l/s).

Various water quality parameters are shown on figure 18. Suspended sediment concentration varied with discharge; background concentrations vary from 30 to 150 mg/l, but suspended sediment exceeded 5,000 mg/l with the peak discharge on 6/29. As would be expected, a variety of other parameters varied with discharge and sediment load. Products associated with soils (sediment) and runoff such as organic-N and ammonium-N reached their highest concentrations (35 and 2.5 mg/l respectively) concurrently with the peak sediment discharge (figure 18). Relatively insoluble products such as potassium (K), phosphorous (as phosphate PO_4), and iron also reached maximum concentrations during these runoff peaks, whereas they were at minimal values during the baseflow-interflow dominated periods.

Atrazine (and other pesticides) also reached its maximum value with the sediment-water discharge maximum of 6/29; atrazine concentrations rose from 2.8 μ g/l on 6/27-28 to 6.6 μ g/l in the 6/29 peakflow.

In contrast, the highly soluble products such as NO_3 and Cl are out of phase with these runoff-related parameters. These soluble compounds show minimum concentrations during runoff and maximum values in stream discharge which is related to shallow-groundwater base flow (and direct tile drainage). Nitrate (figure 19) is directly out-of-phase with organic-N, for example. With the peak runoff-discharge of 6/29 organic-N reaches a maximum concentration of 35 mg/l, while nitrate reaches its minimum value of 6.2 mg/l (1.4 mg/l NO_3 -N).

Conversely, samples from the morning of 6/30, during elevated base-flow discharge, showed that the concentration of organic-N in the stream was only 0.95 mg/l, while the nitrate concentration of Boog-D rose to 68 mg/l (15.3 mg/l, NO_3 -N). During this same time, with high rates of infiltration and shallow groundwater flow, the nitrate concentrations in tile-drainage water reached their maximum concentrations; BTLU-W (just upstream from Boog-D) rose from about 95 mg/l, before these events, to a peak of about 140 mg/l (figure 19). It is interesting to note that pesticide concentrations remained relatively high, and Bladex and Lasso were first detected in the stream-water, during this period of elevated, shallow groundwater flow.

Nitrate concentrations in surface-waters continued to fluctuate with changes in discharge: Boog-D dropped again, to 11 mg/l with the added runoff on 7/1,

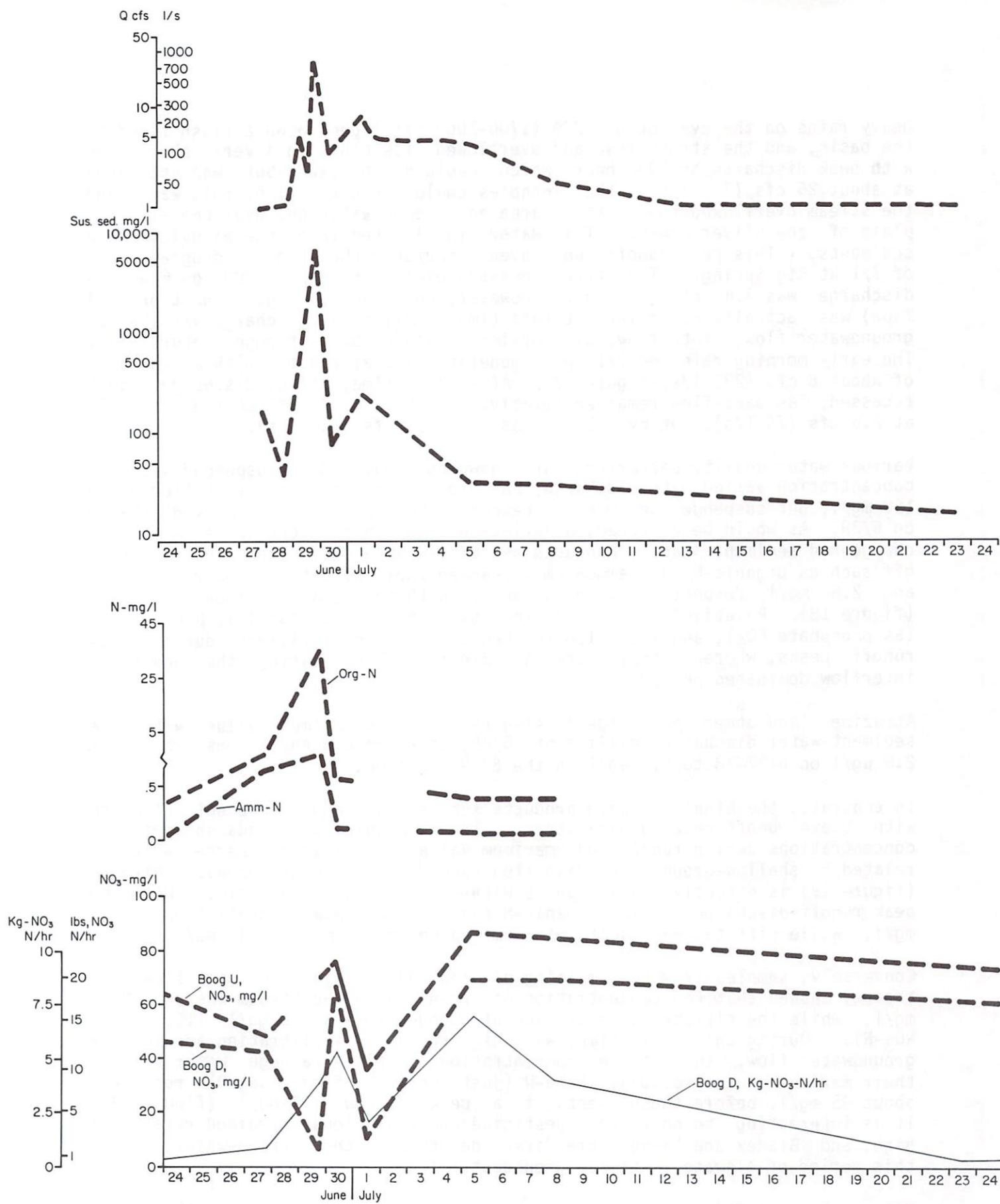


Figure 18. Surfacewater discharge and water-quality at Boog D, which drains into sinkholes (see figures 3 and 4).

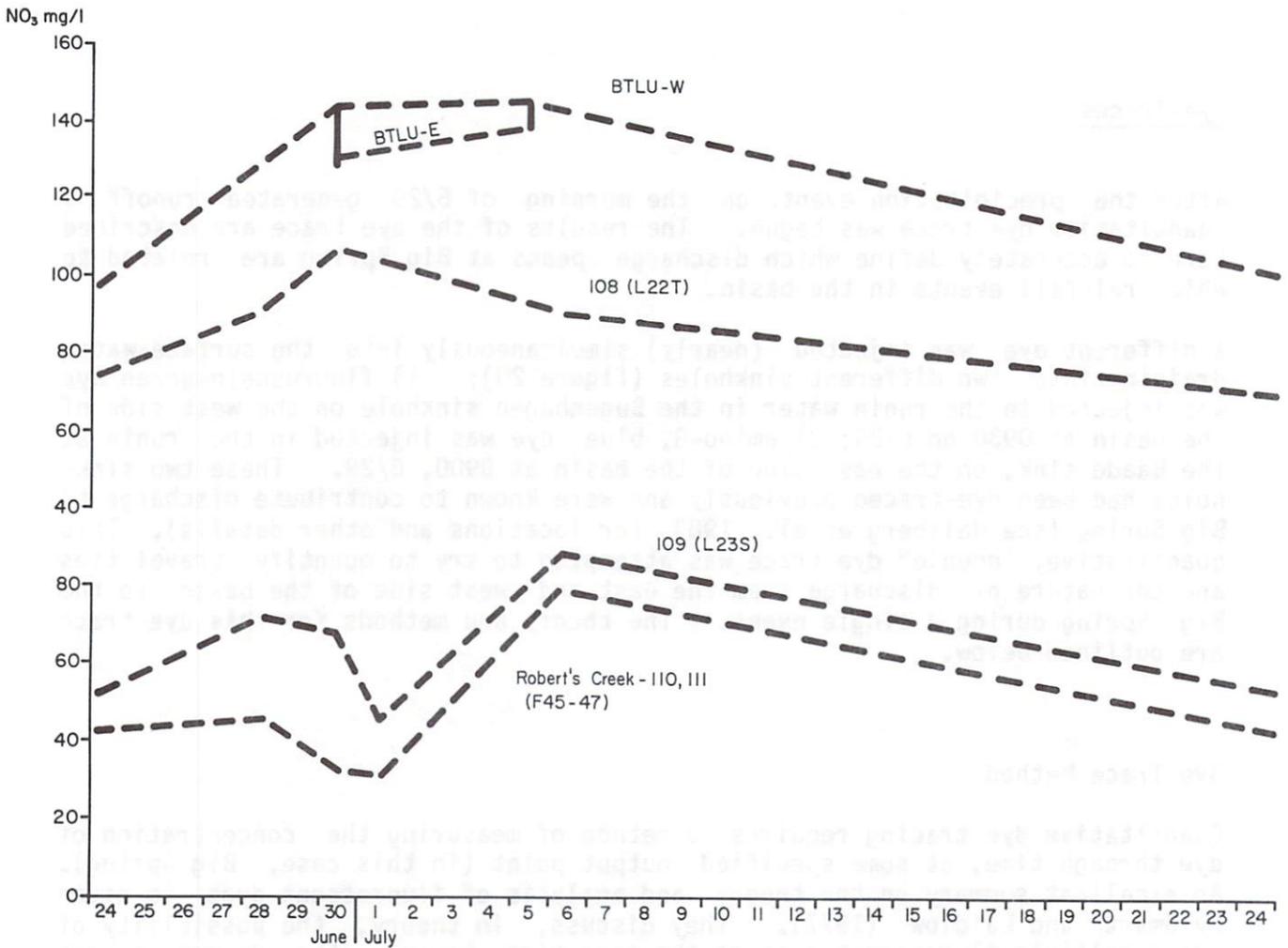


Figure 19. Nitrate concentrations in tile drainage water (BTLU, L22T) and surface water (Silver Creek, L23S; and Robert's Creek) during mid-summer event.

and then rose again to over 70 mg/l with base flow again becoming dominate (figure 18). Figure 19 shows nitrate concentrations from intermittent sampling from larger streams, such as Roberts Creek. These concentrations show different timing of minima because it takes longer for the flood flows to pass through these larger streams.

Nitrate concentrations from the tile lines and surfacewaters all remain quite high, and relatively constant, during the prolonged base-flow recession during the next week, and continuing to the end of July. Figure 18 also shows the calculated discharge of NO₃-N (in kg/hr) at Boog-D. While concentrations remain constantly high, loads decrease substantially after 7/5 as the volume of water discharged declines. This indicates a marked decline in shallow groundwater (or infiltration-related) discharge.

Dye-Traces

After the precipitation event on the morning of 6/29 generated runoff a quantitative dye trace was begun. The results of the dye trace are described here to accurately define which discharge peaks at Big Spring are related to which rainfall events in the basin.

A different dye was injected (nearly) simultaneously into the surface-water draining into two different sinkholes (figure 20): 1) fluorescein-green dye was injected in the runoff water in the Bugenhagen sinkhole on the west side of the basin at 0930 on 6/29; 2) amino-G, blue dye was injected in the runoff at the Baade sink, on the east side of the basin at 0900, 6/29. These two sinkholes had been dye-traced previously and were known to contribute discharge to Big Spring (see Hallberg et al., 1983, for locations and other details). This quantitative, "double" dye trace was attempted to try to quantify travel times and the nature of discharge from the east and west side of the basin to the Big Spring during a single event. The theory and methods for this dye trace are outlined below.

Dye Trace Method

Quantitative dye tracing requires a method of measuring the concentration of dye through time, at some specified output point (in this case, Big Spring). An excellent summary on the theory and analysis of fluorescent dyes is given by Smart and Laidlaw (1977). They discuss, in theory, the possibility of using multiple fluorescent dyes at the same time, however, they do not present any actual studies where this has been done. This method will work if the excitation and emission wavelength-bands of the dyes differ, so that the effects of one dye can be filtered out while the fluorescence of another dye is measured.

As described in Smart and Laidlaw (1977), a Turner, Model 111, filter fluorimeter was used for this dye trace. With the proper combination of filters and dyes, the concentration of one dye will not affect the measured concentration of another. The two dyes used in this dye trace were fluorescein (CI acid yellow 73), a green dye, and amino-G acid (7-Amino 1, 3 Naphthalene disulphonic acid), a blue dye. Primary and secondary filters for the fluorescein analysis were Kodak Wratten numbers 98 and 55, respectively. These filters removed the effects of the amino-G acid. Primary and secondary filters for the amino-G acid analysis were Kodak Wratten numbers 18 and 98, respectively. These removed the effects of the fluorescein. A 10% neutral density filter was also used because it provided the best range of intensities for the dye-filter combinations being used.

Standards for the initial calibration of the fluorimeter were made using Big Spring water collected during mid-June. This was done so that the standards reflected the fluorescence caused by the dyes, plus the background fluorescence caused by the dissolved and suspended solids that characterize Big Spring water. The fluorescein was more affected by background fluorescence than the amino-G.

Standards were constantly run, concurrent with samples from the spring to maintain calibration. The Big Spring samples were generally run in triplicate and averaged (if no anomalous samples appeared).

On 7/1, when the "new water" arrived at Big Spring, with its high sediment loads (discussed in a subsequent section), the water-samples began to produce very strange, enigmatic results for dye concentrations. Because of the high suspended-solids concentrations, the samples were allowed to settle (in a dark, protected area) for about two hours. After this time, stable, repeatable results were obtainable, however, the estimated concentrations for the fluorescein were extraordinarily high (often between 500 and 1,000 $\mu\text{g}/\text{l}$). The water remained murky even after settling and it was suspected that suspended colloids and organic materials might be affecting the results. Thus, some topsoil and loess were mixed with the "background" water (from Big Spring, from 6/29) which had been used to make up the standards. The mixture was made up to approximate the suspended solids load of the new samples. This mix was agitated and then analyzed. These samples produced the same initial erratic results as the new Big Springs samples. After settling for two hours they produced very stable, repeatable background values in the fluorimeter. These new background values were considerably higher than the "standard water" had been, but in the same range as the water currently discharging from the Big Spring. Thus, this new turbid water was decanted and stored and used to make a new set of standards. The dye concentrations in the remaining samples was estimated from the calibration of these new standards.

During this time, until sampling stopped, each sample was analyzed with the prior two samples, as well as with the standards, so that a direct comparison could be made. Thus, even though the turbidity was interfering (particularly with the fluorescein), and producing apparently higher concentrations, the relative differences between samples is assumed to be a valid approximation of changes.

The amount of dye recovered was also calculated from the discharge and concentration data. Calculations indicated that approximately 100% of the Amino-G dye was recovered but the calculations indicated that several times more fluorescein was recovered than was actually input. This was expected from the problems previously discussed. Suspended sediment and organics can interfere in the wavelengths where fluorescein fluoresces, to a much greater extent than in the wavelengths where amino-G is sensitive.

Discussion of Dye Trace Results

Figure 21 shows the measured dye concentrations at Big Spring, in relation to the Big Spring discharge. At the time the dye was injected there was a steady discharge (over one cfs; 28 l/s) into the Bugenhagen sink. However, on the east side of the basin, even after five inches (127 mm) of rain, little runoff was yet occurring. A small volume of water was running into the Baade sink, but it was not a substantial flow. However, this is common for this portion of the basin, where the piezometric surface in the aquifer is depressed far below the landsurface (see Hallberg et al., 1983). Even when runoff is generated in the eastern sinkhole basins it seldom "runs" very far before it simply

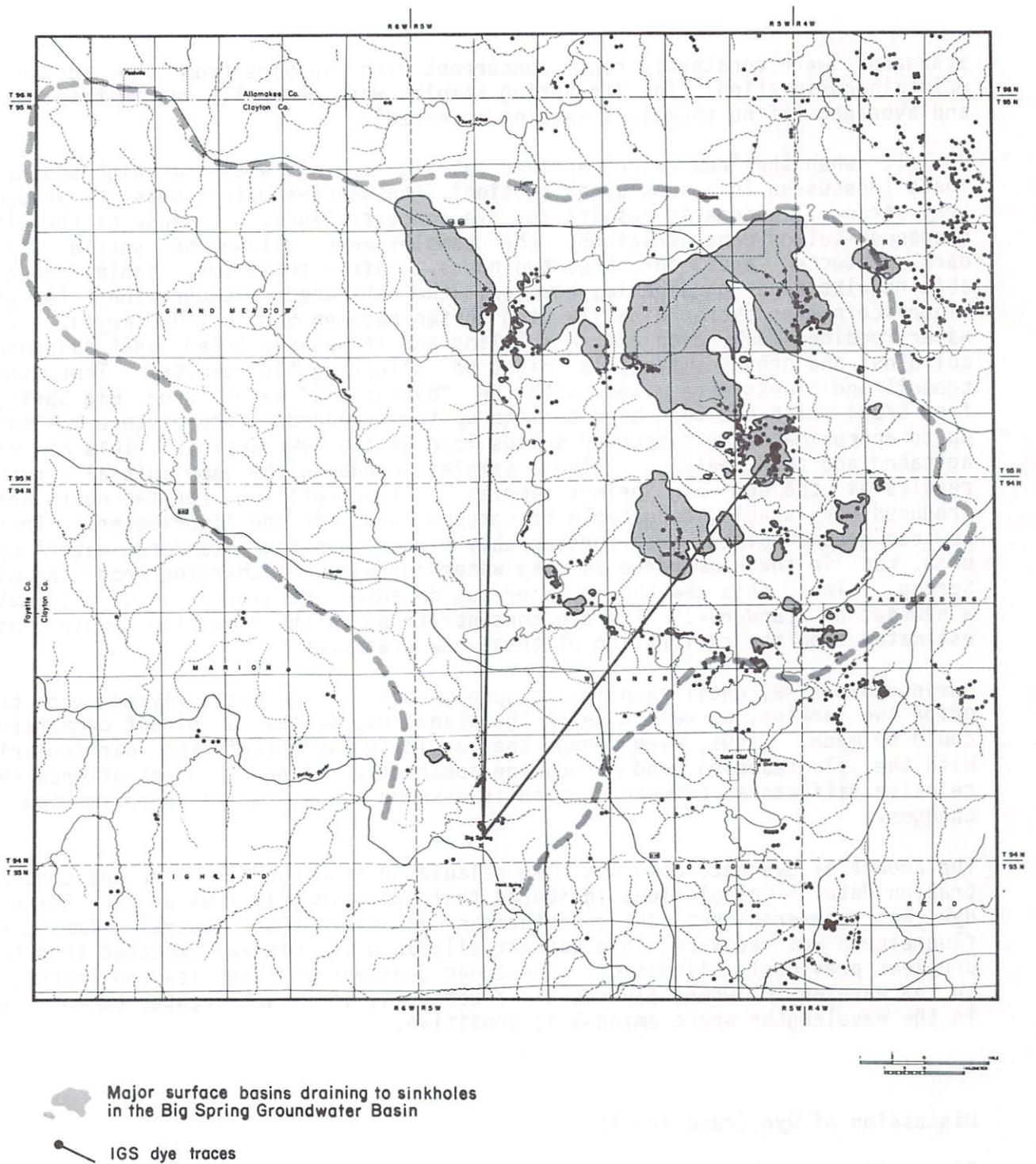


Figure 20. Locations of sinkholes and major sinkhole surface-drainage basins; location of sinkholes used for dye-input during dye traces; and idealized (straight-line) dye flow path to Big Spring.

infiltrates into the soil and rock.

Figure 21 shows the concentration of the dyes in the groundwater at Big Spring over time, and in relation to the Big Spring hydrograph. The arrival of the dye clearly illustrates that the 6/30 hydrograph peak (peak discharge of about 110 cfs; 3.1 cms) was generated by the rainfall-runoff on the morning of 6/29.

The discharge at Big Spring began to rise about 18 hours after runoff (runin) began, and peak discharge occurred 25 hours later. The first arrival of dye from the west side of the basin occurred about 19 hours after injection and the maximum peak concentration occurred nearly coincident with the discharge peak, about 22 hours after injection. Following this peak the dye concentration does not decline in a smooth recession. Rather, during the hydrograph recession the dye concentration was punctuated by wide variations, ranging from 150 to 35 $\mu\text{g}/\text{l}$. When this occurred, the spring was sampled at close intervals (15 to 30 minutes apart) and the samples analyzed in triplicate to substantiate the results. After this fluctuating recession, the fluorescein dye (west side) concentrations rose and remained relatively stable (about 100 $\mu\text{g}/\text{l}$) even during the early phases of the large discharge rise of 7/1. Then concentrations declined sharply as the peak of "new water" arrived during the major discharge event (about 250 cfs; 7.1 cms) on 7/1 (figure 21).

The amino-G dye from the east side of the basin presents a different record. The recorded concentrations of the east-side dye are much lower, and their pattern more attenuated. The first arrival of the dye was about 22 hours after injection, and the first peak concentration arrived 33 hours after injection. A second peak of amino-G dye, (the maximum) arrived on the rising limb of the 7/1 hydrograph event, about 47 hours after dye injection. After this, dye concentrations from the east side also decreased as "new water" arrived on 7/1.

As noted above, the arrival of "new water" on the 7/1 discharge event complicated detection of the dyes. Within the limits of these various problems, however, a few generalizations can still be made. First, dye concentrations dropped to zero (or non-detectable) with the peak arrival of "new water." After this a few "slugs" of water with low concentrations of both dyes still arrived (simultaneously). The last positive detection of dye occurred on 7/2 at 0030 hours, about 63 hours after injection.

Interpretation of the Dye-Trace Results

The quantitative dye trace results present some additional insights into the behavior of the karst-groundwater flow system in the Big Spring basin. The first arrival of dye--19 hours from the west side and 22 hours from the east side--show how rapidly some of the runin-conduit flow water may travel. The sinkholes are approximately 8.6 miles (13.8 km; west side) and 7.7 miles (12.4 km; east side) away from Big Spring, in a simple "straight-line" distance. These data corroborate past, qualitative dye traces which showed that dye from these two sinkholes arrive at Big Spring in less than 24 hours. The time to the peak concentrations (22 hours, west side; 33 hours, east side) indicate minimum (runin-conduit flow) groundwater velocities of 9.4 and 5.6 miles/day

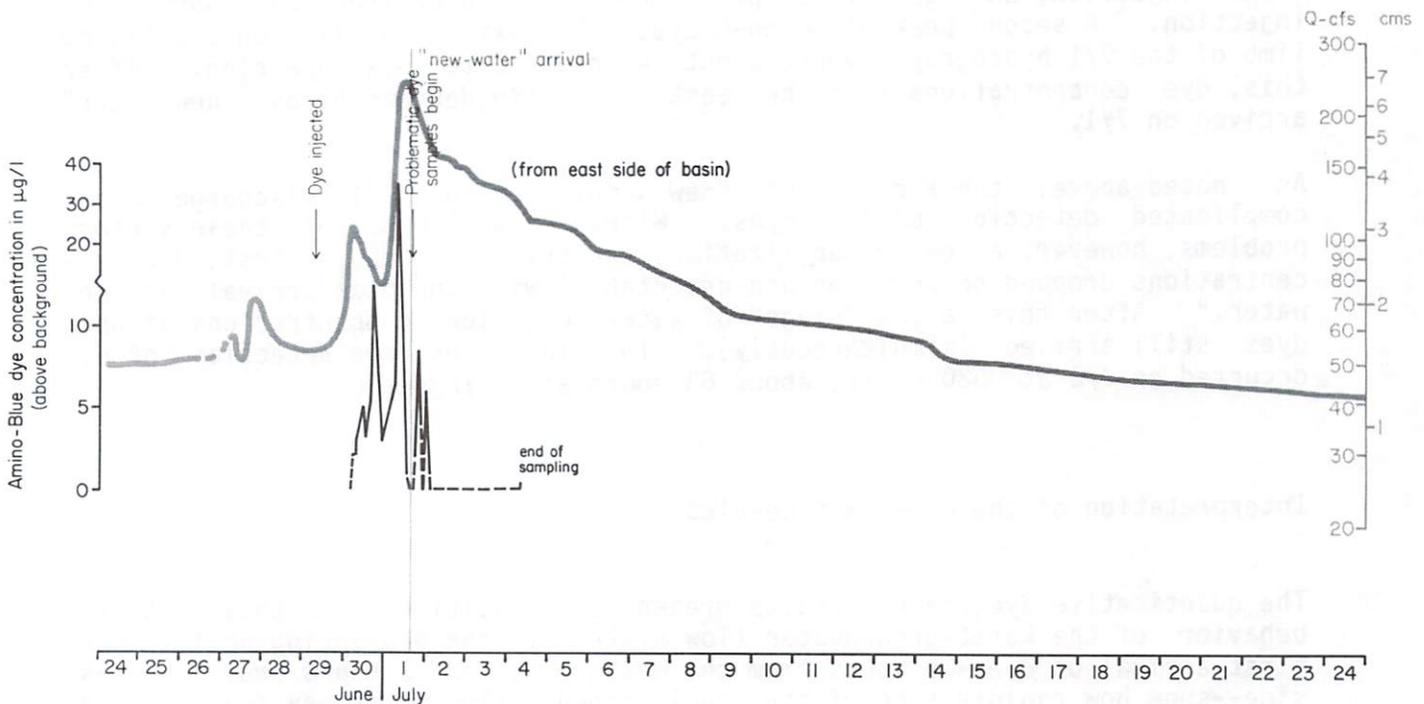
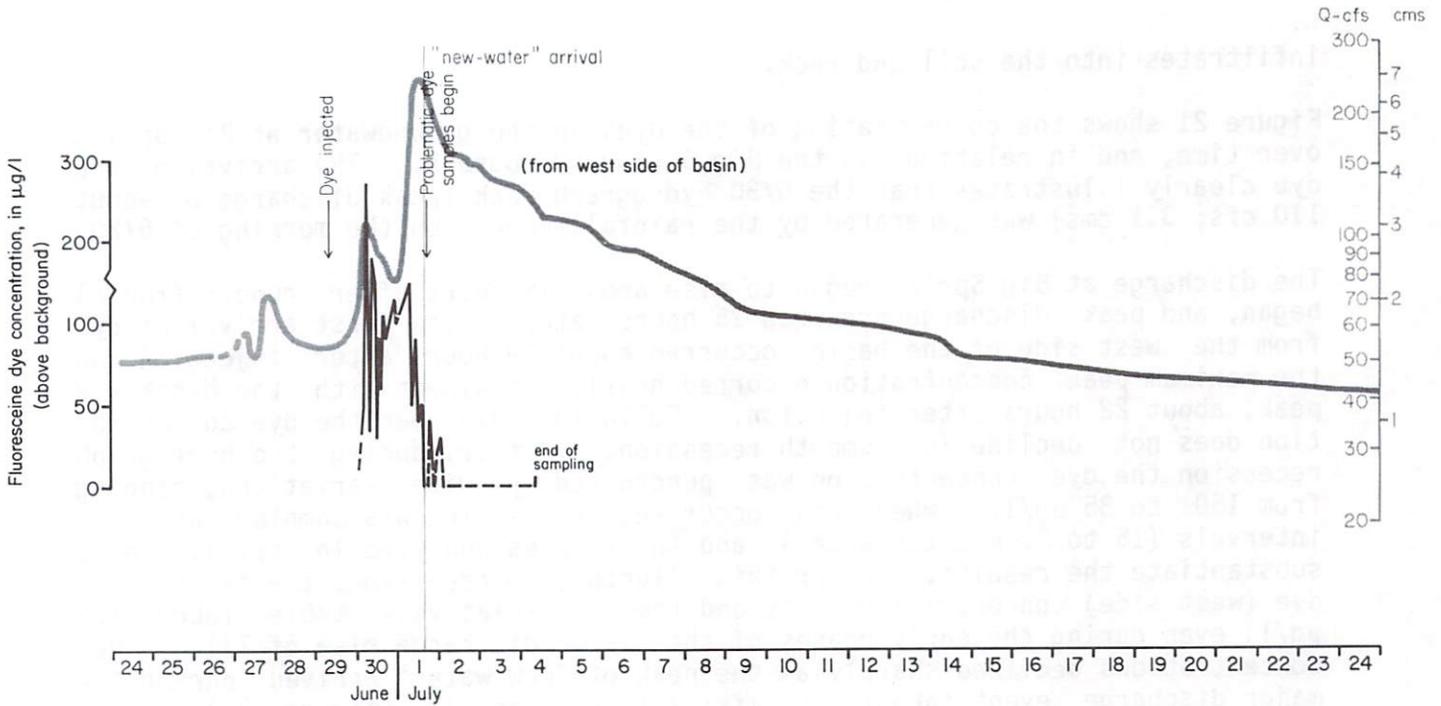


Figure 21. Fluorescent-dye concentration in groundwater at Big Spring from 'double' dye trace during mid-summer event; groundwater discharge record shown in gray for comparison.

(15.1 and 9.0 km/day) or 0.6 and 0.3 ft/sec (0.12 and 0.1 m/s) respectively. The first dye-arrival times indicate minimum rates of 10.9 and 8.4 miles/day (17.5 and 13.5 km/day) or 0.7 and 0.5 ft/sec (0.2 and 0.16 m/s).

As noted by Hallberg et al., (1983; and as will be described in subsequent sections of this report) the arrival of "new (runin-conduit flow) water" at Big Spring is generally marked by coincident maximum concentrations of water quality parameters related to surfacewater transport (e.g., pesticides, suspended sediment, organic-N, P, K, total Fe in water) and minimum concentrations of highly soluble compounds related to infiltration recharge (e.g., nitrate, chlorides, conductivity). The first arrival and peak times for the dyes stand in contrast to these other data. The "new water," related to the 6/30 hydrograph event did not arrive until about 39 hours after runin occurred. This is in the same range of time as the peak-dye arrival from the east side but much longer than the peak time from the west side. As noted by Hallberg et al., (1983) dye traces from other sinkholes often took much longer than from the Bugenhagen and Baade sinkholes. In sum these data indicate that some runin water from individual sinkholes may begin to arrive at Big Spring quite rapidly (within 18-24 hours), but that for the basin as a whole, the maximum impact of runin water will take a longer time to be transmitted through the system (36 to 48 hours). This will be further discussed in subsequent sections.

The great fluctuations in dye concentration from the west side also suggest some of the complexities that occur in the conduit flow system. These variations indicate that water with no-dye, from other sources, such as other sinkholes, losing streams, is injected into the conduit flow, separating the input from an individual point, such as the Bugenhagen sink, into a series of "slugs" of water. Even after the peak of "new water" arrived on the subsequent discharge event of 7/1, a few slugs of "old water," i.e., with dye, were still detected. This indicates that some water was still being displaced through the aquifer system. Such slugs or pulses of water traversing through the karst aquifer system may explain other short-term fluctuations in water-quality that are noted in monitoring karst-carbonate aquifers.

The second peak in amino-G dye, from the east side, which occurred about 47 hours after injection, may represent the displacement of a similar pulse of water. However, because of the limited runin of water which was taking place during dye injection, this peak may also represent a new pulse of water which was input to the system by the subsequent runoff on the evening of 6/29. This dye peak occurs 37 hours after this runin occurred, very similar to the timing for the first peak.

The attenuated dye concentrations, and particularly the much longer time to peak concentrations from the east side of the basin support the previous interpretation of Hallberg et al. (1983). They interpreted that slower travel times of conduit water from the east-side of the basin contribute to the changing rates of hydrograph recessions noted at Big Spring.

Dye was detected until 63 hours after injection. This suggests that at least trace amounts of runin water, and various solutes it contains (e.g., higher concentrations of pesticides, bacteria, etc.) may continue to be transmitted through the groundwater system for at least 2.5 days after a runin event.

Groundwater Discharge

As noted earlier the several rainfalls produced variable amounts of runoff-rinin, which, in turn, produced a series of discharge events at Big Spring. Four discrete events in groundwater discharge (figure 17) occurred in the basin: 1. on 6/27, at 0645 hours, at about 60 cfs (1.7 cms); 2. on 6/27 at 2000 hours, at 73 cfs (2.1 cms); 3. on 6/30 at 0645 at 110 cfs (3.1 cms); and 4. on 7/1, at 1400, at 250 cfs (7.1 cms). The timing of the first rainfall-runoff events are not well defined because IGS crews were not yet in the area. The later events are well defined, as previously described. Thus, the timing between the early runoff-rinin and the initiation of the rise in the Big Spring discharge hydrograph can not be accurately determined, but must be approximately 12 to 14 hours. The rise of the third discharge event began 18 hours after runoff and the rise of event 4 began 29 hours after runoff.

The slope of the rising limb of nearly every large hydrograph peak at Big Spring is very similar. Thus, the larger the discharge event the greater the time there must be between discharge rise and discharge peak, as well as a proportional increase in the time elapsed between runin and peak. Thus, the time from rise to peak for peak 1 was less than six hours (at 60 cfs; 1.7 cms), for peak 2 about seven hours (at 73 cfs; 2.1 cms), for peak 3 about eight hours (at 110 cfs; 3.1 cms), and for peak 4 about 14 hours (at 250 cfs; 7.1 cms). The time from runin to peak for peak 3 was about 26 hours and for peak 4 about 43 hours.

As noted peak 3 was generated by the rainfall-runin which occurred between 0500 and 0700 on 6/29; and peak 4 by the rainfall-runin which occurred between 1700 and 2000 on 6/29 (figure 17). The subsequent smaller rains on 7/1 through 7/3 did generate minor runoff (see previous discussion), but in general added more significantly to infiltration. These runin events were not of significant quantity to cause another rise in discharge, given the high discharges already occurring. However, about 30 to 35 hours after these rains (slightly more time from rain to rise than for peak 4) the recession limb of peak 4 changes slope and becomes nearly flat, holding a nearly constant discharge for several hours (e.g., on 7/2 between 0800 and 1500 hours). Thus, these additional rains appear to contribute to the overall form of the hydrograph recession.

A review of the past discharge records for Big Spring show similar results. All individual discharge events under 150 cfs (4.3 cms) begin their rise in less than 24 hours after rainfall-runin, but few have the resolution of the June-July 1983 events. Where a new discharge peak occurs immediately on the recession of another event each subsequent event seems to have a longer response time, just as noted for the June-July 1983 events. Most of the events over 200 cfs (5.7 cms) had response times between 24 and 36 hours. However, large snowmelt events (previously described) which occurred during low base-flow periods appear to begin to rise in less than 24 hours after runoff. This suggests that the time between runin and rise at Big Spring is in part related to antecedant conditions as well.

The increasing time between successive runin and rise events is anomalous. The successive greater increases in head related to infiltration and runin

water filling conduits should transmit a proportionally greater pressure through the groundwater system and actually cause a more rapid response. This was noted in the discussion of the snowmelt events; an increase in discharge at Big Spring was noted within 9 hours of peak melting, yet groundwater travel times, as indicated by chemical changes, were still in the realm of 21-24 hours. One critical difference may be noted between the 1983 snowmelt-discharge period, and the June-July 1983 events: During the snowmelt discharge fluctuations (when this pressure-wave phenomenon could be observed) the discharge never fell below 85-90 cfs (2.4-2.5 cms). During these other periods, which exhibit an inverse relationship between the timing of runoff and the rise in discharge, such as the June-July events, the discharge between events fell below 80 cfs (2.4 cms). This suggests that at these lower discharges the conduits are not full enough to show this pressure response. Hopefully, further observations will help clarify these relationships.

Groundwater Quality

Groundwater samples were collected as often as hourly (but at least every three hours) during much of this monitoring period. These samples were analyzed for a variety of parameters. The first parameter which will be discussed is specific conductance (SpC) because it integrates the effects of changing solute concentrations and also presents a rather simple and straight forward picture of the events.

The change in conductance at Big Spring, in relation to the discharge is graphed on figure 22. Few SpC measurements were made prior to 6/29, and only minor changes were noted. During the discharge event of 6/30 SpC fluctuated somewhat, and overall decreased slightly. Again, only a slight decrease occurs on the rising limb of the 7/1 peak-discharge event (figure 22), and it is not until well into this event that SpC shows a marked decrease, dropping from 670 to 450 $\mu\text{mhos}/\text{cm}^2$ in less than 7 hours. It is at this point that all water-quality parameters indicate that the "new," surface runoff water arrives at Big Spring. As will be shown, this is where the water-quality parameters related to surfacewaters reach a maximum and parameters, such as SpC which relate to dissolved constituents transported through infiltration are at minimum values, as shown on figure 22. Note that arrival of the "new water" does not take place until after the discharge has peaked. The water discharged on the rising limb of the event has the characteristics of water that was already in the conduit system. Unlike in a surfacewater system where floodwaters can simply add to water in the channel or overflow the channel, in the conduit-flow, groundwater system this water has to be pushed out of the way, or displaced before the "new water" can arrive. This water is what Hallberg and others (1983) termed "displaced-conduit water," or simply displacement water.

The SpC rises more slowly as discharge recesses, as the runoff water component passes through the system. On the recession limb SpC became relatively stable, with one noticeable rise on about 7/5, coincident with one of the last flat areas on the recession limb of the discharge event. Note that SpC returns to about the same value as before this series of discharge events took place.

The discussion of the remaining water-quality data will be divided into two general categories: 1. parameters most strongly related to the runin, conduit flow component; and 2. parameters most strongly related to the infiltration, or base-flow component.

Run-in, Conduit Flow Components:

1. Suspended Sediment

Perhaps the most obvious parameter related to surfacewater runin is suspended sediment. Figure 23 graphically shows the suspended sediment concentration over time, against the discharge hydrograph, and figure 24 shows the discharge rate (kg or lbs/hr) for suspended sediment at Big Spring. During base-flow discharge the suspended sediment concentration in the groundwater from Big Spring is negligible, averaging about 10 to 25 mg/l (within the error of measurement of these low concentrations). This changes radically with large discharge events, however.

Little change could be measured in the suspended sediment concentration related to the small discharge events 6/27, although the turbidity of the water did increase. With the larger event of 6/30 however, suspended sediment concentration increased to nearly 100 mg/l. The sediment concentration continued to increase in the displacement water, on the rising limb of the 7/1 event, and then peaked with the "new water" arrival, at over 4,000 mg/l. Note that this is approximately the same suspended-sediment concentrations as recorded in the surfacewaters running into the sinkholes in the basin (figure 18).

At this peak of suspended sediment concentration and water discharge the sediment discharge rate was about 96 tons/hr (or 87,000 kg/hour; see figure 24). The trend of sediment concentration parallels the water discharge trend, and thus the sediment discharge graph mimics the concentration. After the peak, the concentration drops off nearly as quickly as it rose. The data show a minor increase in suspended sediment on 7/3, which is related to the rainfall, runin event in the basin on the morning of 7/1 (figure 18).

During the smaller discharge event of 6/30, the total suspended sediment discharged through Big Spring was about 16.2 tons ((15,000 kg). During the larger event of 7/1, to recession at 100 cfs (2.8 cms) on 7/4, the total suspended sediment discharged at Big Spring was over 1,122 tons or 1,000,000 kg. This averages out to about 371 tons/day (336,000 kg/day); or 15.5 tons/hr (14,000 kg/hr). It is no wonder that sediment loads are a serious problem for the ICC fish hatchery operation.

For discussion and perspective, if the total suspended sediment load for this one event (7/1-7/3) is proportioned back over the sinkhole basins (where much of the sediment runs into the system) this amounts to an equivalent of 0.15 tons/acre of sediment during this single event. Again, for perspective, the total suspended sediment discharged during July 1983 was about 1,150 tons (1,043,000 kg). About 98% of this was discharged during 7/1-4, during the peak flows.

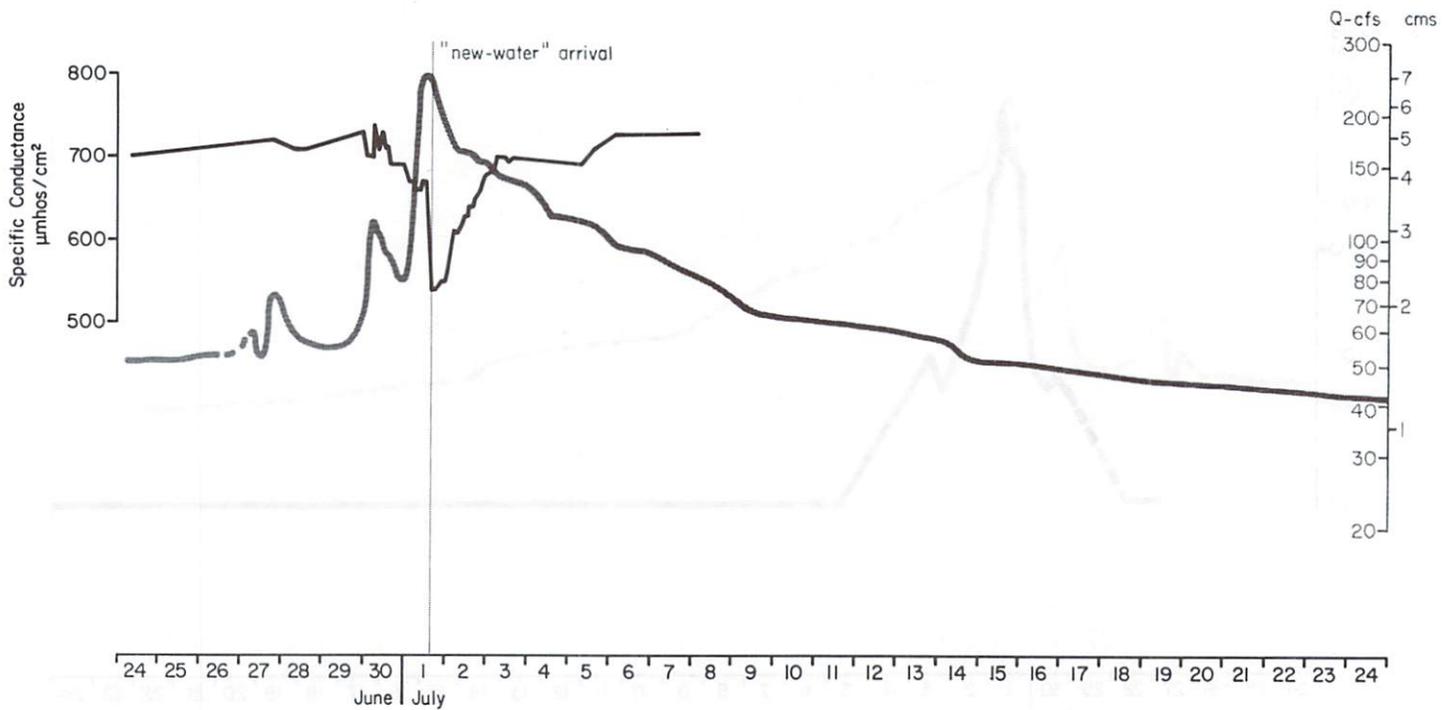


Figure 22. Specific conductance of the groundwater at Big Spring during mid-summer event; groundwater discharge shown as gray background for comparison.

Though these figures provide perspectives, they also must be clarified. First, note that the sediment concentration rises directly with discharge. Although it does peak with the "new water" arrival as marked by other parameters it is not as discrete as the abrupt change in SpC; i.e., concentrations rise during the displacement water as well. This is because considerable sediment is stored in the "fluvio-karst" conduits, and the large discharges remove large amounts of this stored sediment. Some of the sediment is derived directly from the rocks which form the conduits. The sand fraction of some of the sediment samples is dominated by dolomite rhombs and abraded carbonate rock fragments. On the other hand, chemical analyses of the sediment samples show that dieldrin and sometimes atrazine are attached to the sediment (clay and organic) particles. The dieldrin in particular (because it is strongly adsorbed) suggests that some of the sediment has not had a long residence time in the conduit system; the use of aldrin (dieldrin) stopped in about 1973. The proportioning of the sediment over the sinkhole basins is not entirely accurate either because of the residence time issue. Also, some sediment will enter the system through solutionally-widened joints and fractures. However, the major volume of sediment must be delivered into the conduit-system through losing streams, such as described in the Bugenhagen basin. The fact that sediment concentration peaks match with other surfacewater, runoff parameters also suggests that some of the sediment load courses directly through the entire conduit system to be discharged at Big Spring during

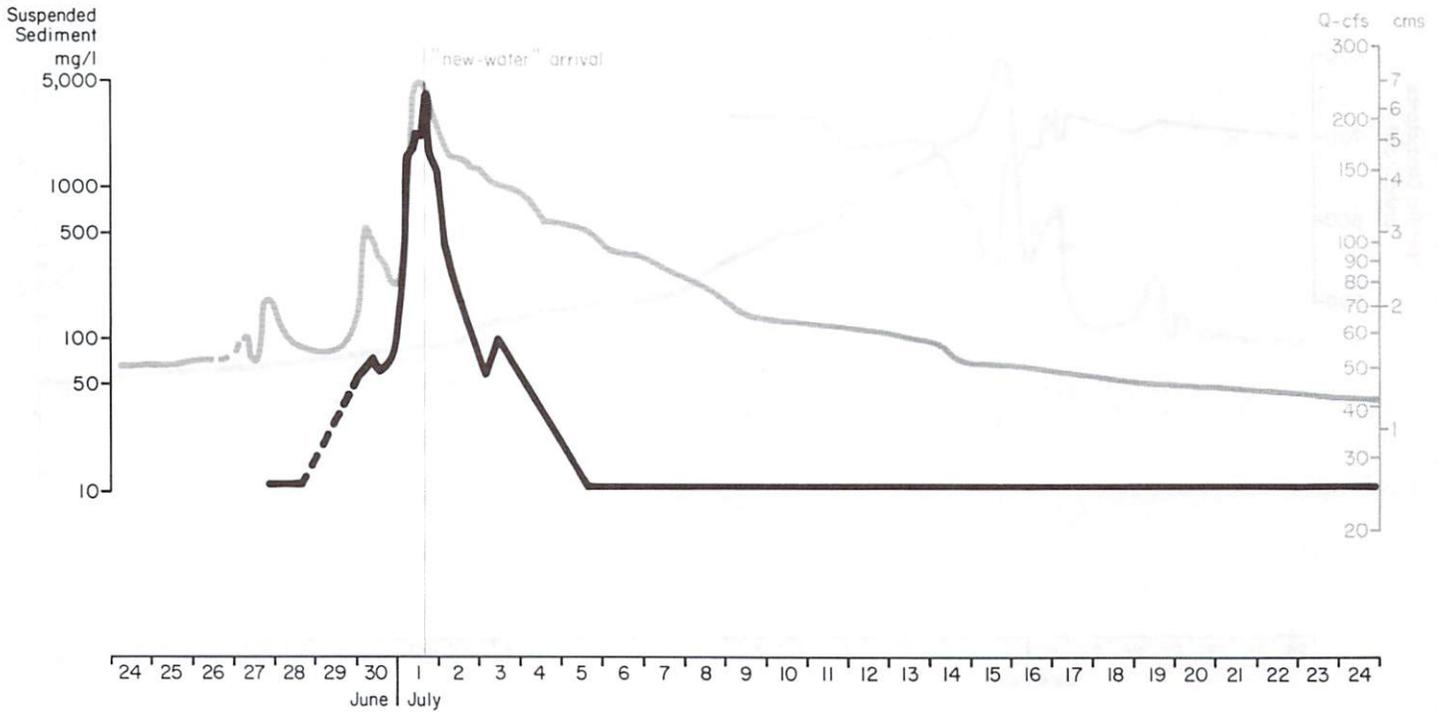


Figure 23. Suspended-sediment concentration in groundwater at Big Spring during mid-summer event.

such high flow events. (This is also illustrated by the discharge of relatively fresh corn stalks and corn cobs at Big Spring, during high flows.) In some respects the sediment load at the spring can be thought to be a minimum because the coarser sediment delivered into the system (some bed load) probably cannot be transported through the system, nor "buoyed up" to be discharged at Big Spring.

2. Organic-N, Ammonium-N

Organic and ammonium-N are common constituents in surfacewater but generally not groundwater. During stable, base-flow periods they are not detectable in the groundwater discharging from Big Spring. During the 6/27-7/4 discharge events N-series (analyses for $\text{NO}_3 + \text{NO}_2\text{-N}$, Organic-N, and ammonium-N) samples were collected at Big Springs from 6/27 through 7/25. The results are shown on figure 25.

The pattern of concentrations, with time and discharge, are similar to the suspended-sediment data. Organic-N shows some increases with every discharge event, but peaks (6.7 mg/l) with the "new water," just slightly after peak discharge. Ammonium-N only appeared during the 6/30 and 7/1 events, and shows a double-peak around the same time as organic-N, but is

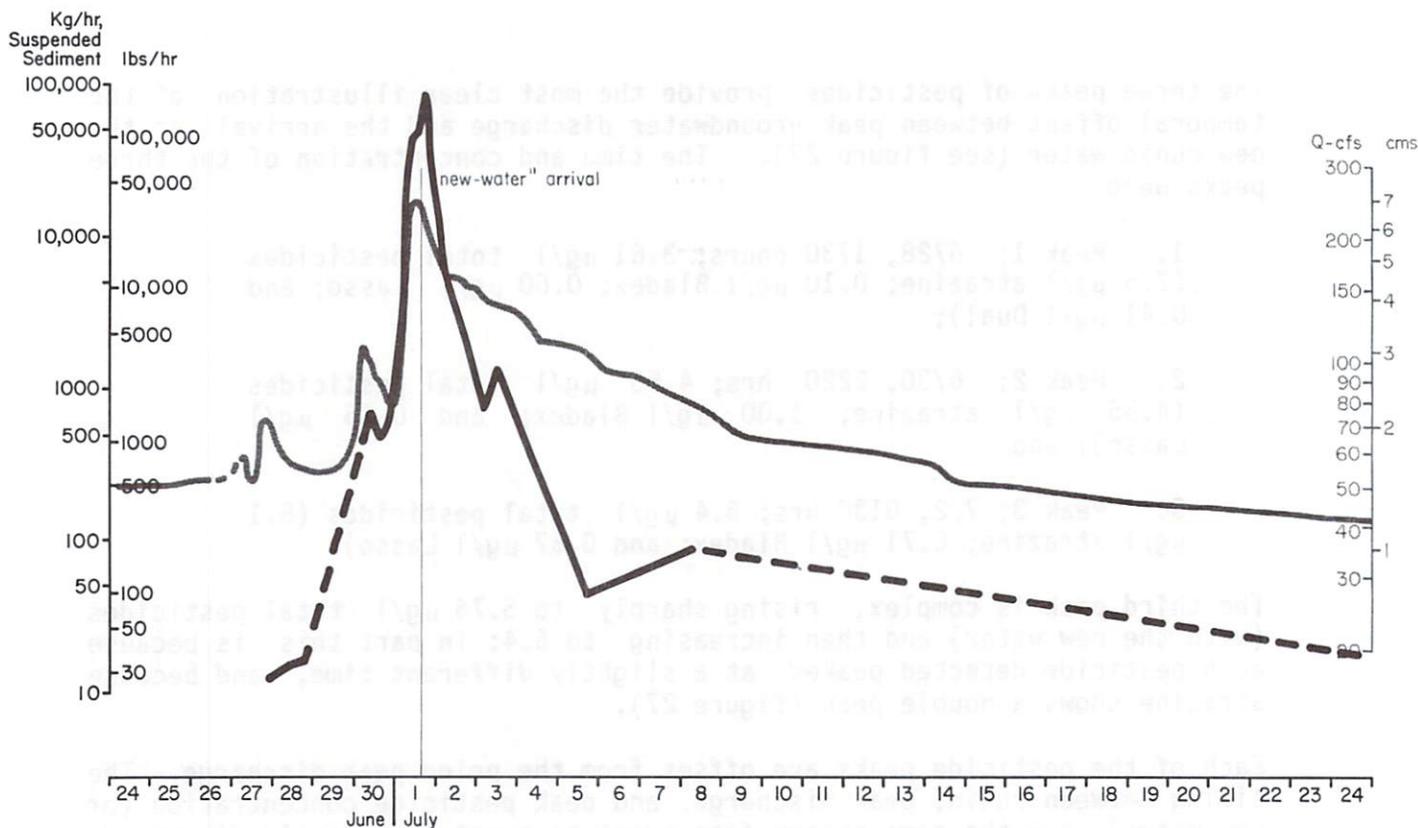


Figure 24. Mass of suspended-sediment discharged with groundwater at Big Spring during mid-summer event.

still at very low concentrations (0.7 mg/l maximum). Both decline rather quickly and by 7/3 were no longer detectable. The concentration of organic-N can be clearly related to the concentration of suspended sediment (figure 26), as is often the case in surfacewaters.

3. Pesticides

Immediately prior to the discharge events the only pesticide detected in the groundwater at Big Spring was atrazine. It was present in its typical background concentrations of about 0.2 $\mu\text{g/l}$ (see Table 9 and Appendix 1). This was a base flow period and the discharge of atrazine was averaging about 22 g/day (0.05 lbs/day). After runoff of surfacewater began, several other pesticides appeared in the groundwater, and three distinct peaks of pesticide concentration occurred after the peak discharges (see figure 27). In addition to atrazine, the herbicides Bladex (cyanazine), Lasso (alachlor), Dual (metolachlor), and the insecticide Dyfonate (fonofos) were detected in groundwater during this period (Table 9).

The three peaks of pesticides provide the most clear illustration of the temporal offset between peak groundwater discharge and the arrival of the new runin water (see figure 27). The time and concentration of the three peaks were:

1. Peak 1; 6/28, 1730 hours; 3.61 $\mu\text{g}/\text{l}$ total pesticides (2.5 $\mu\text{g}/\text{l}$ atrazine; 0.10 $\mu\text{g}/\text{l}$ Bladex; 0.60 $\mu\text{g}/\text{l}$ Lasso; and 0.41 $\mu\text{g}/\text{l}$ Dual);
2. Peak 2; 6/30, 2220 hrs; 4.55 $\mu\text{g}/\text{l}$ total pesticides (4.55 $\mu\text{g}/\text{l}$ atrazine; 1.00 $\mu\text{g}/\text{l}$ Bladex; and 0.45 $\mu\text{g}/\text{l}$ Lasso); and
3. Peak 3; 7/2, 0130 hrs; 6.4 $\mu\text{g}/\text{l}$ total pesticides (5.1 $\mu\text{g}/\text{l}$ atrazine; 0.71 $\mu\text{g}/\text{l}$ Bladex; and 0.57 $\mu\text{g}/\text{l}$ Lasso).

The third peak is complex, rising sharply to 5.76 $\mu\text{g}/\text{l}$ total pesticides (with the new water) and then increasing to 6.4; in part this is because each pesticide detected peaked at a slightly different time, and because atrazine shows a double peak (figure 27).

Each of the pesticide peaks are offset from the prior peak discharge. The timing between runin, peak discharge, and peak pesticide concentration (or new water) show the same change from event-to-event, previously discussed. Pesticide peak 1 occurs about 17-21 hours after discharge peak 2 of 6/28, and about 24-36 hours after runin. Pesticide peak 2 occurs about 16 hours after the discharge peak (6/30) and 31 hours after runin. Pesticide peak 3 occurs about 11 hours after peak discharge, but about 54 hours after runin.

The maximum concentrations of the various pesticides recorded were: 5.1 $\mu\text{g}/\text{l}$ atrazine, 1.2 $\mu\text{g}/\text{l}$ Bladex, 0.63 $\mu\text{g}/\text{l}$ Lasso, 0.62 $\mu\text{g}/\text{l}$ Dual, and 0.11 $\mu\text{g}/\text{l}$ Dyfonate. The maximum concentrations all occurred during the largest event, late 7/1 or early 7/2. Note, again, that the maximum concentrations recorded are essentially the same as the maximums noted in surface-water discharging into sinkholes.

Suspended sediment collected during the maximum discharge was also analyzed for pesticides that may be attached to the sediment (or organic matter). The sediment showed concentrations of 2.6 $\mu\text{g}/\text{g}$ atrazine and 0.6 $\mu\text{g}/\text{g}$ total pesticides. The concentrations of the pesticides in the water varied, to an extent, directly with the suspended sediment load. As shown on figure 28, above about 1.0 $\mu\text{g}/\text{l}$ the total pesticide concentration tended to increase with suspended sediment concentration, although the relationship is not as strong as between organic-N and sediment (figure 26). Below about 1.2 $\mu\text{g}/\text{l}$ there is no relationship, and such pesticide concentrations are in the range of base-flow concentrations where suspended sediment is barely measureable.

Figure 29 shows the discharge of atrazine, over time (in g/hr or lbs/hr), during the events. In sharp contrast to the base-flow rate, which averages about 22 grams per day (0.05 lbs/day), during the discharge events, with the high pesticide concentrations in the runin-conduit flow water, the rate peaked at 120 g/hr (0.26 lbs/hr). During the high flow days of

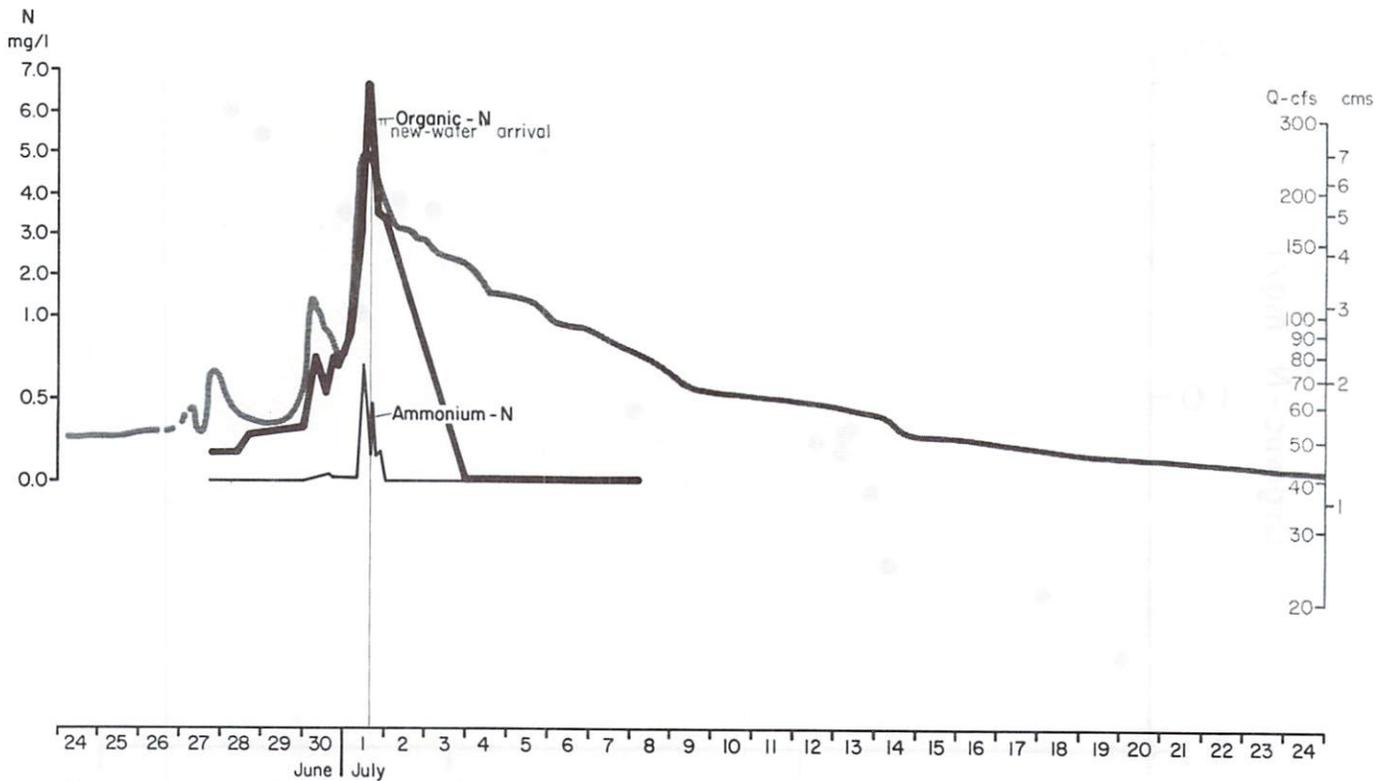


Figure 25. Concentration of organic-N and ammonium-N in groundwater at Big Spring during mid-summer event.

7/1 and 7/2 the atrazine discharged in groundwater was about 1.5 kg/day (3.4 lbs/day). For the period between 6/27 to 7/11 on the recession the total load of atrazine discharged was 5.36 kg (or 11.8 lbs). The atrazine discharged in this two-week period equals over 80% of the calculated atrazine discharge for the prior water-year (Hallberg et al., 1983).

As is apparent on both the pesticide concentration and load diagrams, with the passage of runin-water, the pesticide concentration (and load) quickly return to base-flow concentrations, just as the suspended sediment and organic-N did. By 7/08 atrazine concentrations had declined to 0.42 $\mu\text{g/l}$ and by 7/12 to 0.25 $\mu\text{g/l}$. On 7/5 was the last sample with any pesticide other than atrazine; atrazine, 0.58 $\mu\text{g/l}$ and Bladex 0.21 $\mu\text{g/l}$ (figure 27). This is about 3 days after the last runin event. This may be the last vestige of runin water. The dye trace data suggests that some traces of runin water may reside in the system that long. Conversely, this may simply be from infiltration. As discussed with the high infiltration and shallow groundwater flow that took place, atrazine, Bladex, and Lasso were all noted in shallow groundwater-interflow, and tile-drainage water in the Bugenhagen basin. In any case, it is typical for the Big Spring basin, that pesticide species other than atrazine are only found in groundwater during periods characterized by runin events.

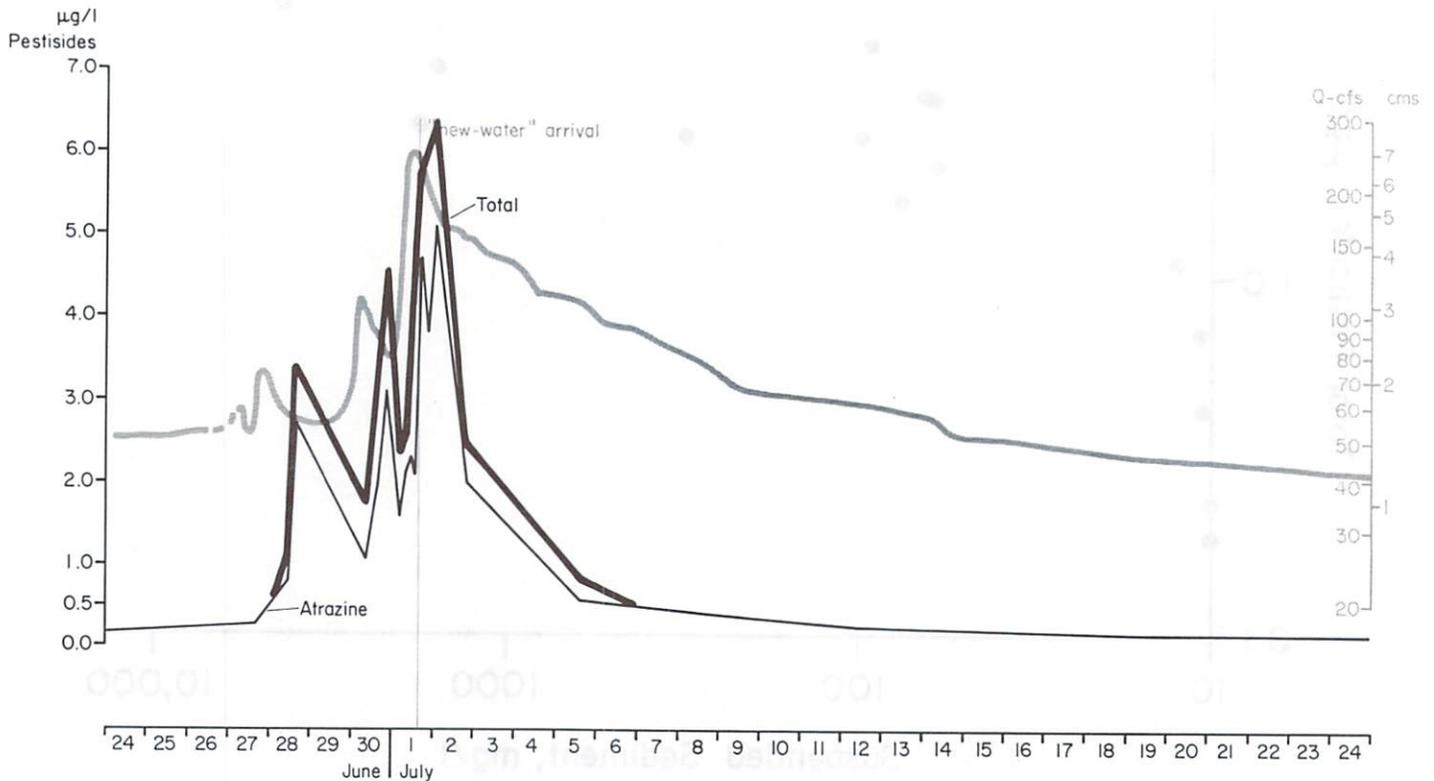


Figure 27. Total pesticide and atrazine concentration in groundwater at Big Spring during mid-summer event.

The 7/1 discharge event was large enough that it was even reflected in groundwater temperatures. Usually only snowmelt events have a measureable affect on the groundwater temperatures at Big Spring. The influx of this late June-early July warm surfacewater caused groundwater temperatures to rise from about 10.1°C up to 11°C (50°-52°F).

Infiltration Component

1. Nitrates

As discussed for specific conductivity, dissolved mobile constituents, which have their highest concentrations in the infiltration component of the groundwater recharge, show an inverse trend to the runin, conduit-flow components. As with SpC they show minimum concentrations, i.e., maximum dilution, with the arrival of the new, runin-water. The most important constituent of this component (for the present study) is nitrate. The concentration of nitrate in the groundwater at Big Spring is shown on figure 31.

The concentration of nitrate shows a very complex pattern with time. This results from the complex interplay of the multiple discharge events and

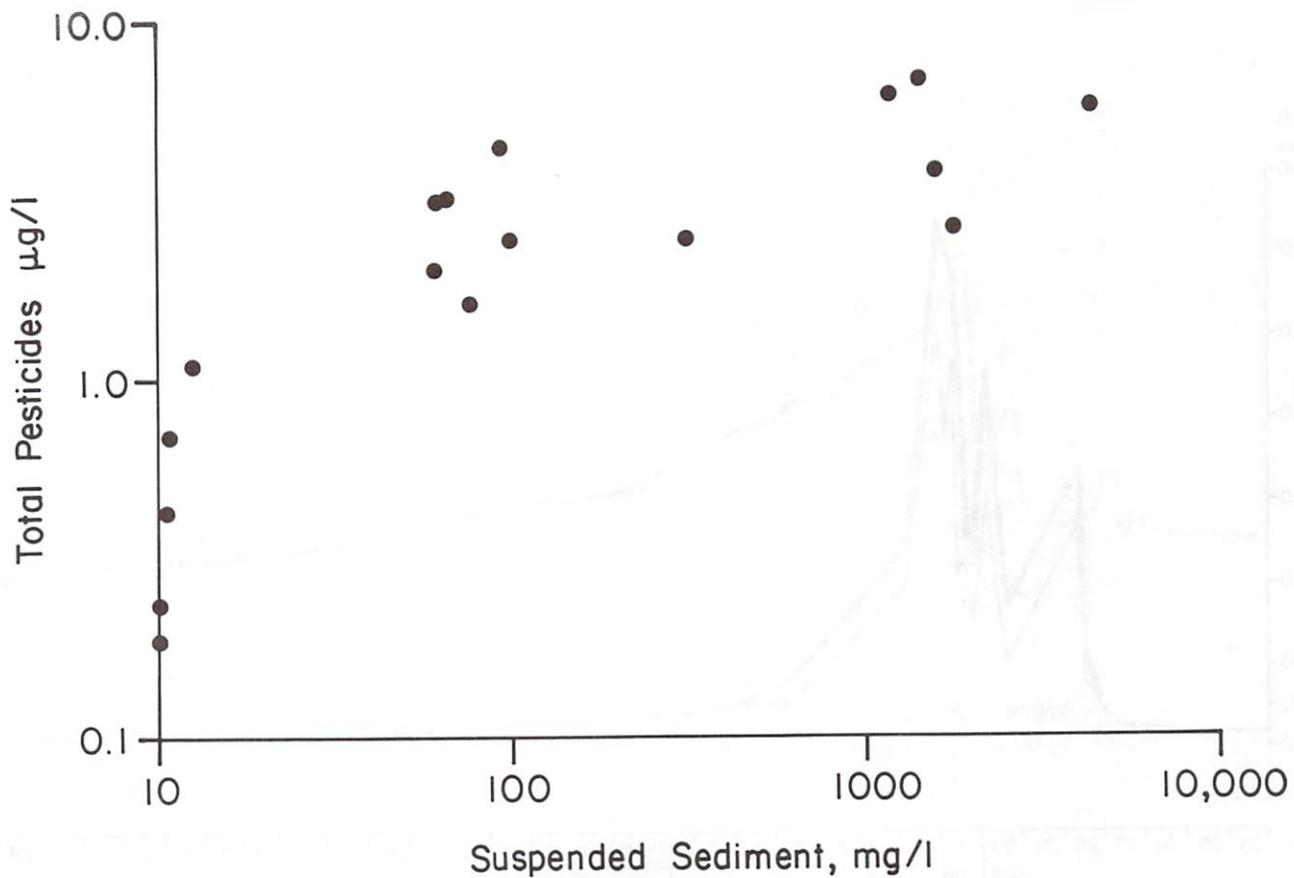


Figure 28. Total pesticide vs. suspended sediment concentration in groundwater from Big Spring, during mid-summer event.

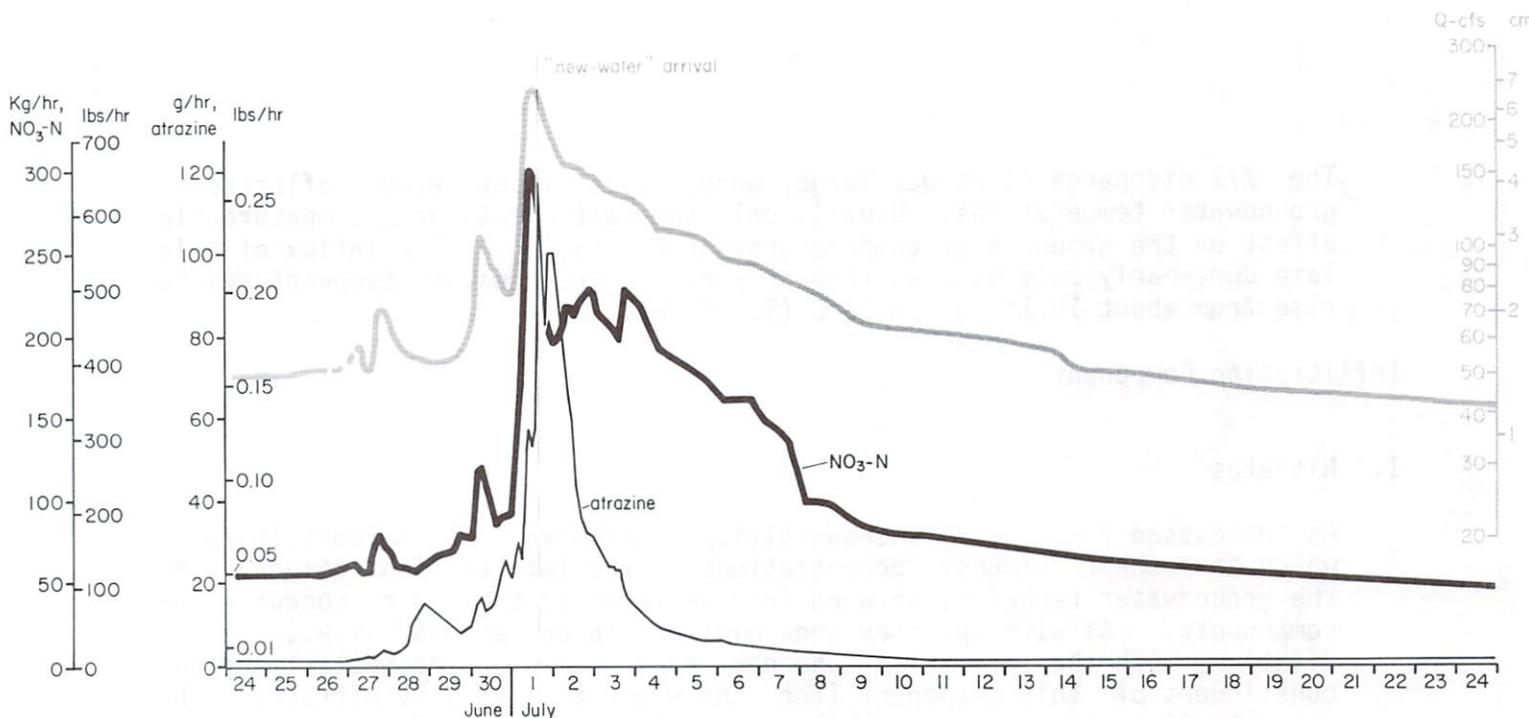


Figure 29. Mass of atrazine and NO₃-N discharged with groundwater at Big Spring during mid-summer event.

the mix of infiltration, base-flow and runin, conduit-flow waters being discharged. In the base-flow period, immediately prior to 6/27 (figures 2 and 31), nitrate concentrations were stable at about 44-45 mg/l. During the first discharge rise of 6/27 detailed monitoring began, and nitrate concentrations rose slightly (figure 31) and then dropped sharply (to 41 mg/l) after the second discharge peak on 6/27. As noted previously, this was thought to indicate the arrival of runin water related to this event; roughly coincident with the nitrate minima were increases in turbidity, pesticide concentrations, K and total Fe, a minor rise in organic-N, and a drop in other soluble ions, such as chloride and sulfate. After this the nitrate concentration rose sharply to a "plateau" at about 56 mg/l, where it remained for about 8 hours.

This plateau terminated with a sharp decline, during the 6/30 discharge event. The concentration fluctuated and again reached values of about 54 mg/l on the rising limb of the large 7/1 discharge event. At first this rise in concentrations may appear strange, but this is in the displacement water on the rising limb and does not represent new, runin water.

With the arrival of the new, runin water nitrate concentration again declines sharply to a minimum level (42 mg/l), coincident with the peak concentrations of the runin parameters. As discharge declined on the falling limb of the event, nitrate concentrations rose sharply again, from 42 mg/l to 55 mg/l in 9 hours. The nitrate concentrations continue to rise, in a series of plateaus: going from 57 mg/l to 65 mg/l in 6 hours and then stabilizing for about 20 hours; then rising from 63 mg/l to 74 mg/l in 5 hours (at 2345 hours, 7/3). The nitrate concentration remained at this level (72-74 mg/l), from 7/4 through 7/7, and then the plateau terminated; the nitrate concentration decreased overnight from 72 mg/l (7/7) to 54 mg/l (7/8, at 0 740 hours). The nitrate concentrations gradually declined as recession continued to the end of July (figure 31), but not until 7/29 did nitrate concentrations return to the 44 mg/l level that they were at prior to these events. The nitrate plateaus that occurred after the 7/1 minima are roughly coincident with the "flat" areas on the recession curve that were related to the minor precipitation events (principally, infiltration events that occurred on 7/1 through 7/3), in the prior discussion (figure 31).

The discharge of nitrate-N in the groundwater from Big Spring is shown on figure 29 (kg and lbs/hr). The discharge rate of nitrate-N shows a complex pattern also, with peak loads occurring when high concentrations and high water discharge rates coincide. Again, in contrast to baseflow discharge rates of about 110-120 lbs (50-55 kg) $\text{NO}_3\text{-N/hr}$, during these large events rates reached 660 lbs (300 kg) $\text{NO}_3\text{-N/hr}$. During 7/1 through 7/4 about 11,000 lbs, or 5.5 tons, (5,000 kg) of $\text{NO}_3\text{-N}$ were discharged daily in groundwater. During the period 6/27 to 7/11 over 103,200 lbs or 51.6 tons (over 46,800 kg) of nitrogen (as nitrate) were discharged.

Figure 29 generally shows the out-of-phase relationship between the discharge of nitrate and atazine. In general, as pesticide loads were rising and reaching maxima, nitrate loads were declining to minimal values. Unlike parameters related to the runin components, nitrate-N discharge stayed quite high during the early recession, because of the high nitrate concentration plateaus. Nitrate-N discharge dropped sharply overnight,

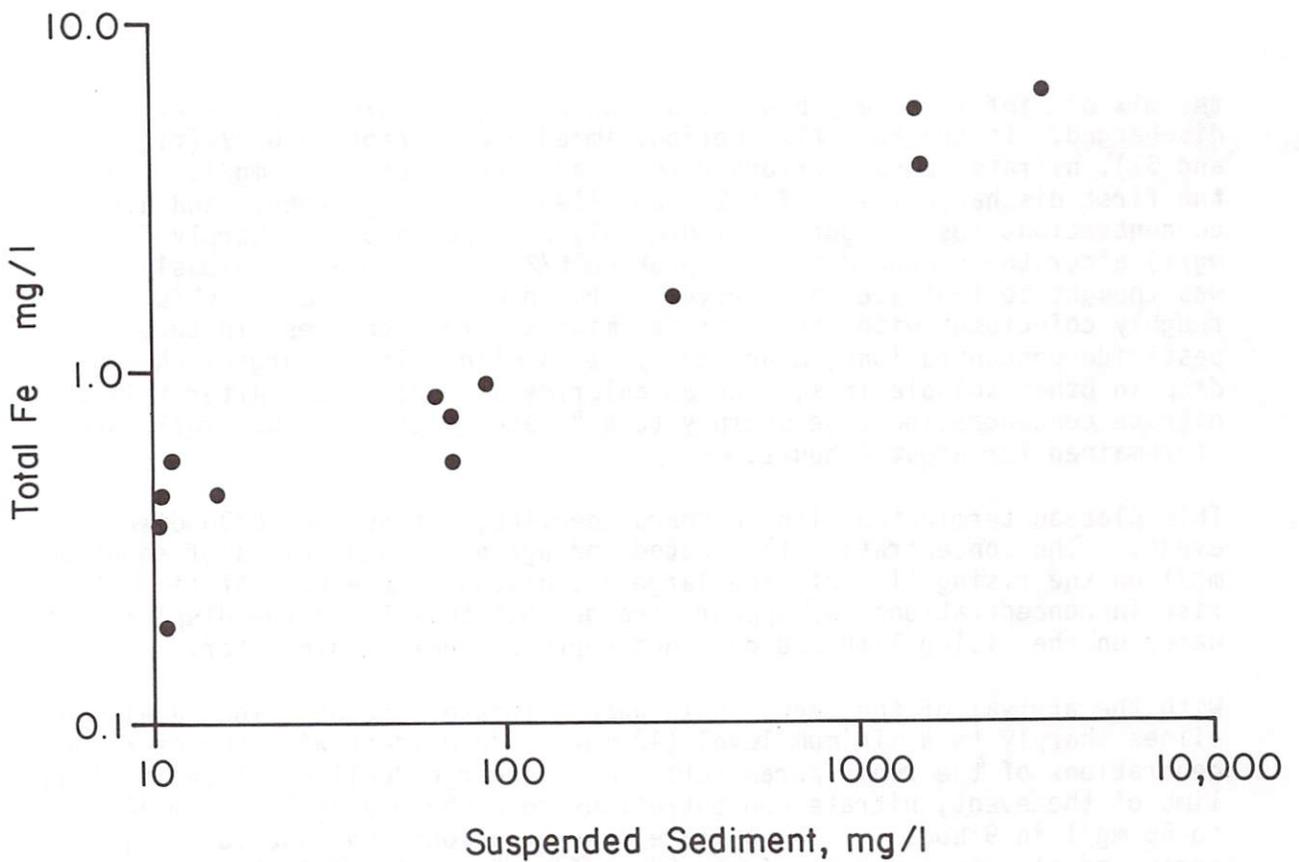


Figure 30. Total iron vs. suspended sediment concentration in groundwater at Big Spring, during mid-summer event.

from 7/7 to 7/8, with the end of the last nitrate-concentration plateau.

Discussion of the Nitrate Data

Two of the complexities of the nitrate concentrations at Big Spring warrant further discussion: 1. the sharp fluctuations that occurred; and 2. the nitrate "plateaus." Before discussing these features it is necessary to briefly review some data from the basin.

As previously discussed, the first 5-6 inches (125-150 mm) of precipitation generated very little runoff. Much of this water infiltrated, replenishing the soil moisture deficit; some was obviously lost to evapotranspiration. This infiltration water mobilized significant amounts of nitrate, stored in the soil profile (in soil water, under tension), which was then displaced in the infiltration recharge from subsequent rains. This is shown by two direct lines of evidence: 1. changes in nitrate concentrations in tile-drainage water; and 2. changes in nitrate concentrations in surfacewaters, during

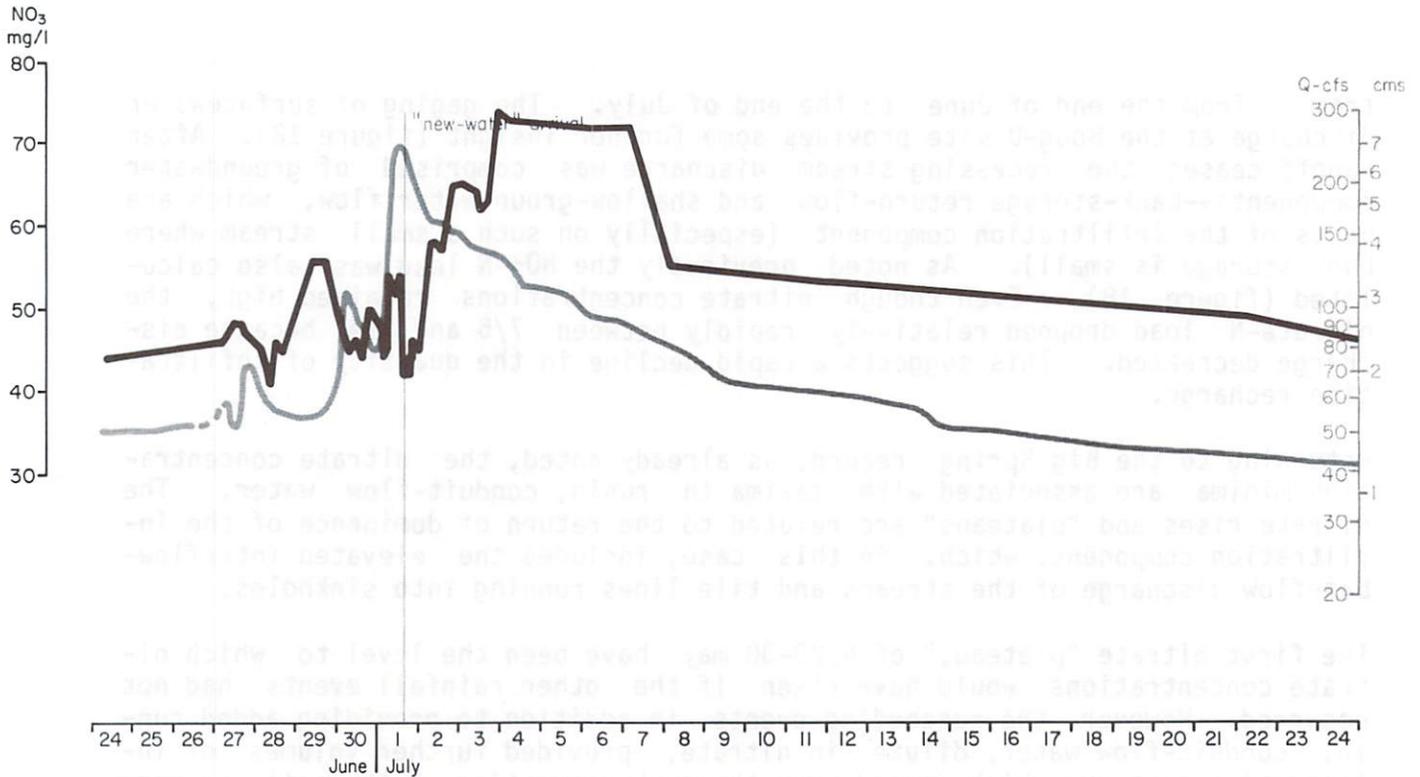


Figure 31. Nitrate concentration in groundwater at Big Spring, during mid-summer event.

periods when their discharge is dominated by shallow groundwater (e.g., baseflow and interflow periods). Unfortunately, these portions of the hydrologic system were not monitored in the same detail as Big Spring. Hence, the exact timing of these changes is not as well documented.

As tile drainage discharge increased (from empirical observation) the nitrate concentration (particularly from tiles draining fertilized corn) increased 25 to 60%, by 6/30 (e.g., figures 19 and 6). The concentrations reached maximum levels between 6/30 and 7/4, some tiles showing concentrations of over 140 mg/l. Concentrations remained relatively high, and then recessed to the end of July (e.g., figure 19 and 6).

Surfacewater nitrate concentrations fluctuated with discharge, as discussed, from very low, diluted, values during runoff events, to much higher values during baseflow-interflow periods. Again, across the period of the discharge events, nitrate concentrations in the surfacewaters increased from 25 to 100%, during these periods dominated by groundwater flow (e.g., figure 18 and 19). In the smaller streams, in particular, nitrate concentrations remained relatively constant to the end of July (e.g., figure 18).

Thus, the nitrate concentrations in the infiltration component, in the shallow-flow system, rose sharply and decreased more slowly over this time

frame, from the end of June to the end of July. The gaging of surfacewater discharge at the Boog-D site provides some further insight (figure 18). After runoff ceased the recessing stream discharge was comprised of groundwater components--bank-storage return-flow and shallow-groundwater flow, which are parts of the infiltration component (especially on such a small stream where bank storage is small). As noted previously the $\text{NO}_3\text{-N}$ load was also calculated (figure 18). Even though nitrate concentrations remained high, the nitrate-N load dropped relatively rapidly between 7/5 and 7/9 because discharge decreased. This suggests a rapid decline in the quantity of infiltration recharge.

Returning to the Big Spring record, as already noted, the nitrate concentration minima are associated with maxima in runin, conduit-flow water. The nitrate rises and "plateaus" are related to the return of dominance of the infiltration component, which, in this case, includes the elevated interflow-baseflow discharge of the streams and tile lines running into sinkholes.

The first nitrate "plateau," of 6/29-30 may have been the level to which nitrate concentrations would have risen if the other rainfall events had not occurred. However, the succeeding events, in addition to providing added runin, conduit-flow water, dilute in nitrate, provided further volumes of infiltration recharge which caused more thorough saturation of the soil and more efficient displacement of the soil water and solutes. Hence, nitrate concentrations continued to rise, in a series of stepped, "plateaus," on 7/2, 3, and 4. These steps are nearly coincident with the flat-portions of the discharge recession, which were caused by the added small rainfall events previously described.

Of note are the sharp fluctuations in nitrate on 6/30 and 7/1 between the peak of the 6/30 discharge event and the arrival of "new water" with the 7/1 event. As described for the dye-trace, the arrival of runin waters appears at times, to be punctuated by slugs of identifiable runin water, separated by other water. The nitrate data further support this thought: the various nitrate minima in this interval correspond with the periods of dye-concentration maxima, and conversely the nitrate maxima correspond with periods of dye minima (east-side) or stable dye concentration levels (west-side).

As noted in the prior discussions, the sharp increase in nitrate noted on the rising limb of the "plateau" may be explained as the relatively rapid passage of runin, conduit-flow water followed by new infiltration water, enriched in nitrate which is displaced from "storage" in the previously unsaturated parts of the soil profile. The much more difficult feature to interpret is the falling limb of the plateaus. This must invoke a mechanism that promotes a 25 to 50% decrease in nitrate concentration in 12 to 24 hours. Rapid declines in nitrate are easy to explain with the influx of surfacewater during a discharge event, but this does not occur at the termination of the plateaus. In both the April and the July plateaus the termination occurs abruptly about 3.5-4 days after the last significant precipitation.

Perhaps a mechanism can be found in the observations within the basin. As noted in prior discussions, the nitrate concentrations in the tile-drainage water (proxy of infiltration recharge water) rise immediately preceding the nitrate plateaus. Over the long term (of a few weeks) nitrate concentrations in the tile-lines decline and reflect changes similar to those noted at Big

Spring (e.g., figure 6), but the real time perspective of the 24-hour declines in the nitrate plateaus are not reflected. (Concentrations did decrease slightly in some tiles, e.g., site L22T. However, the tiles were not sampled in enough detail at this time to accurately determine the timing or rate of their drop in nitrate concentration.) As noted (figures 18, 19, and 6) nitrate concentrations in the basin decline slowly until toward the end of July, and do not reflect the abrupt drop in concentration that occurs between 7/7 and 7/8 at Big Spring. However, the relatively abrupt decrease in nitrate-N load, because of declining discharge, does occur between 7/5 and 7/8. Also, by this time tile-drainage had essentially ceased on the east side of the basin (in the Sass sub-basin, figures 3 and 5). As discussed, this suggests a relatively abrupt decline in shallow groundwater flow (infiltration recharge). The termination of the nitrate plateaus may mark the relatively rapid cessation of the free gravity-drainage, or infiltration, from the near surface, which was displacing water enriched in nitrate. This component recharges the groundwater system both through direct infiltration and through shallow base-flow, interflow, stream discharge into sinkholes. The gradual recession in nitrate concentrations that follows suggests that the water that continues to recharge the aquifer and come out of storage has a lower nitrate concentration, but becomes proportionally greater than the high nitrate source water.

As discussed for rapid-infiltration changes during the April and the snow-melt period, the rapid response time indicates that the source of these effects must be the sinkhole basins and other areas where the bedrock is very shallow beneath the land surface, and in relatively direct connection with the soil. This is indicated because the high-nitrate infiltration water must infiltrate, and be transported quickly to Big Spring, in large part, through the conduit-flow system; the high-nitrate water arrives within 24 to 48 hours of a discharge peak, often immediately following the recession of runoff, conduit-flow water.

Another factor limiting interpretations of the nitrate plateaus is that their termination occurs during gradual recession of groundwater discharge. For example, the termination of the last July plateau does not coincide with any of the sharper drops in water discharge that mark the end of the "flat" periods on the hydrograph record (figure 31). Rather the termination of the "nitrate" plateau simply occurs during gradual recession; discharge only decreased from 84 cfs (2.38 cms) to 77 cfs (2.18 cms) as nitrate dropped from approximately 72 to 55 mg/l (in 13 hours between 1820 hours, 7/7/83, and 0740 7/8/83). This is very similar to the termination of the April plateaus. In both these instances, where the termination was completed (i.e., without a subsequent event) nitrate concentrations dropped abruptly about 20 mg/l as discharge gradually decreased about 5-10 cfs (0.15 -0.30 cms). It is interesting that in all instances the termination occurred as discharge recessed within a range from about 90 cfs (2.5 cms) to about 75 cfs (2.1 cms). (Ongoing monitoring, in water-year 1984 shows similar relationships.)

This suggests that there is not an abrupt termination of a particular source of water--just an abrupt change in the amount of nitrate contained in the water. In essence it suggests the nitrate plateaus simply mark the passage of a "slug" (albeit, a large one) of high-nitrate water. A simple two component mixing model of the change in nitrate concentration over this small change in discharge would suggest that, if the high nitrate concentrations were caused by a unique source of water, that the nitrate concentration in

that water would have to be on the order of 200 to 400 mg/l. This seems unreasonable because it is considerably above the highest values recorded in any of the tile-lines monitored in the basin. (Even if an offset relationship is assumed between the timing of the chemical change and the discharge change unreasonably high values are implied.)

Although other rises and falls in nitrate concentration have occurred at Big Spring related to obvious infiltration-discharge events, they have not been as dramatic in magnitude, nor as abrupt in timing as the April and July nitrate "plateaus." A review of monitoring records show that few events have had sufficiently high magnitude (i.e., recessions beginning above 90 cfs, or 2.5 cms) to generate such phenomenon. Only in November, 1982 were conditions appropriate, and indeed a sharp increase in nitrate concentrations is noted (figures 1 and 2) but monitoring was not detailed enough to define this event.

In summary, the various observations about the nitrate "plateaus" suggest the following:

1. The timing of the beginning of the nitrate "plateaus," in relationship to the discharge hydrograph, and the sharp rises in nitrate concentration in tile-lines and other shallow groundwater base-flow to streams show that the plateaus are related to the infiltration, base-flow component of the groundwater discharge at Big Spring. During recession of a discharge event this component is comprised of true infiltration recharge and groundwater base-flow and tile-line discharge into sinkholes. This is only logical because the "storage area" for high concentrations of the very mobile nitrate ion is in the pore water in the unsaturated soil profile and immediately subjacent materials.
2. The rapid "arrival" or beginning of the nitrate "plateaus" suggest that the source areas must be sinkhole basins and other high-infiltration, shallow-bedrock areas, where infiltration water, tile-drainage, and stream base flow water can enter, and be rapidly transmitted through the conduit-flow system.
3. The relationships between the fluctuating or gradually declining discharge and the stable portion of the "plateau" and its abrupt termination suggest that the "plateau" is not related to a discrete source of water which also abruptly passes through the system. Rather this suggests that, in large part, the nitrate concentration of the water must change.
4. While tile-drainage water (from the west side of the basin) also shows relatively sharp declines in nitrate concentrations (figure 6), the major decrease does not occur until some time after the termination of the "plateau." Tile drainage, while a proxy of some aspects of shallow groundwater, reflects only the quality and activity of this water in the upper few feet of the soil. Small stream base-flow which integrate somewhat deeper, shallow groundwater movement, also maintains high nitrate concentrations but the total discharge (and hence the volume of high-nitrate water) decreases in the same time frame as the "plateau" termination. Also, in this same time frame

tile-drainage in the eastern sinkhole basin areas essentially ceased. This shows that there is some simple volumetric decrease in the delivery of the high nitrate concentration water. This also suggests a relatively abrupt decline in shallow groundwater recharge, in the proper time frame.

5. The interpretation that we draw from all these lines of inference is that the nitrate plateaus are generated during infrequent, high-magnitude events which are marked by high-rates of infiltration recharge. During these events the soil becomes thoroughly saturated and true piston, or displacement flow takes place--efficiently mobilizing and displacing high concentrations of nitrate through the soil profile and into the groundwater system in the shallow-bedrock, high-infiltration areas, through direct infiltration recharge and by indirect discharge of groundwater base-flow through surfacewater into sinkholes. The terminations of the "plateaus" are caused by the concurrent and rapid decline in the nitrate concentration in this displacement-infiltration water, and the volumetric decline in the indirect recharge. Because there is little perceptible change in the rate of the groundwater discharge recession, there must be little change in the overall rate of recession of the infiltration recharge and diffuse flow. Nitrate, and other less mobile forms of nitrogen (organic-N) are not uniformly distributed through the soil. With high rates of application of N-fertilizers over long periods the N and nitrate tends to occur in high concentration in the surface horizon and generally at some depth, below the rooting zone, in the soil profile or sub-soil materials. How effective the displacement and movement of nitrate is from these zones of concentration will depend on how thoroughly saturated the soil is and how long it remains in that state (contact and residence time). With macropore drainage it is unlikely that displacement is totally effective. Two mechanisms seem to be plausible causes for the termination of the nitrate plateaus. First, as the soil becomes thoroughly saturated the soil water will have time and opportunity for both lateral and vertical movement through the zones of high nitrate concentration in the soil. This will allow the mobilization of the nitrate into the groundwater. As this mass of high-nitrate concentration, infiltration water drains through the soil and into the aquifer, the top of the zone of saturation (water table) declines, gradually lowering the head and discharge of the groundwater system. At some point the water table drops below the zone of high nitrate concentration in the soil. Though the water table, and hence discharge, continue a gradual decline, the water now draining through the soil into the aquifer is no longer in effective contact with the high nitrate concentration zones, and the nitrate content of the recharge water drops sharply. This mechanism must assume that infiltration, in the concept of displacement or piston-flow, is not totally effective in displacing the nitrate.

The second related mechanism may assume that the displacement is very effective. During infiltration drainage through the soil,

as the head lowers, the high-nitrate concentration water may reflect the displacement of much of the nitrate-N available at that time. Concentrations then drop sharply after this pulse of displaced nitrate is delivered into the groundwater system. The water that continues to gradually infiltrate through the soil has a much lower nitrate concentration, and mixes with the other diffuse-flow water, which contains nitrate concentrations in the range more typical (40-50 mg/l) for this time of year. As the soil drains and returns to conditions more conducive to oxidation additional N-species will be mineralized to NO_3 and be available for mobilization during subsequent events.

At first, it may seem unlikely that such events would take place concurrently across the basin. However, the monitoring of tile-drainage water shows that under conditions of widespread rainfall tile-lines respond nearly simultaneously in various settings, in widely separated portions of the basin (see figure 6 for example). This has been observed elsewhere: Baker and others note (1975, p. 411),

"Data from soil and groundwater sampling [sic], the fact that abrupt increases in flow rate can cause abrupt changes in NO_3 -N concentration, and the observation that NO_3 -N concentrations in tile drainage water change simultaneously, all indicate that there are pulses or waves of water passing through the soil profile with different NO_3 -N concentrations. These pulses or waves in drained areas probably are due to a combination of factors such as soil moisture conditions, depth and amount of organic matter, temperature, tillage, and timing and amounts of precipitation and fertilizer applications."

This will be further discussed in the section on tile-proxy monitoring.

6. Another possible contributing factor may be inferred from the discharge hydrograph data. As noted the terminations of the "plateaus" always occur as discharge recesses between about 90 and 75 cfs (2.5 to 2.1 cms). As described in the discussion of the snowmelt period, at discharges of about 85 cfs (2.4 cms) or greater the conduit-flow system appears to be saturated to the extent that it can transmit pressure waves, rapidly increasing discharges at Big Spring as the head in the aquifer increases. Collectively, this may also suggest that as the discharge recedes below about 85 cfs (2.4 cms) that the head in the aquifer may decline, and cross a threshold which allows the return-flow into the conduits of lower-nitrate concentration water, which was displaced into the aquifer, during the preceding intervals of greater head and discharge. (This water would be the "return-flow" water analagous to "bank-storage" water discussed by Hallberg et al., 1983, p. 151-153). This mechanism certainly contributes to the gradual decline in nitrate concentrations which occurs after the termination of the plateau.

This general relationship may also suggest that in this range of discharges the head decline lowers the water table below the source of the high nitrate concentrations in the soil, as discussed in item 5 above, and/or this may imply the cessation of recharge from these rapid infiltration-areas because of the decline in head. However, this in part, infers the termination of a source of recharge water for which there is little evidence, as previously discussed.

2. Other Infiltration Parameters

As mentioned, other parameters also fluctuated with nitrate, and SpC, notably chloride and sulfate, but these parameters were not monitored in such detail. For example, Cl, which is generally present at 18-19 mg/l concentrations, reached a measured minimum of 12 mg/l during dilution at new water. In general, all major ions with the previously noted exceptions of potassium and iron showed lower concentrations in the "new" runoff water because of little interaction with the soil during recharge, and limited interaction with the aquifer itself, because of fast conduit-flow rates. All the data from the mineral scan analyses are tabulated in Appendix 2.

Hydrograph Separation

The discharge hydrograph of the midsummer rainfall event was separated into diffuse-and conduit-flow components using the methods described in the discussion of the snowmelt period (also see Hallberg et al., 1983). The analytical separation is shown in figure 32. Peak-conduit flows of about 160 cfs (4.6 cms) are indicated, almost two thirds of the total discharge. During the major discharge period (6/30/83-7/11/83), about 2,400 acre-feet (2.96 million cm) of water were discharged. Based on the analytical separation, about 1840 acre-feet (2.27 million cm), or 77% of the discharge was infiltration-diffuse flow recharge, with the remaining 560 acre-feet (0.69 million cm) representing surface runoff to sinkholes and conduit flow. Spread over roughly 7,360 acres (2,980 ha) which drain to sinkholes, the conduit-flow system delivered 0.91 inches (23 mm) of runoff, or about 15% of the rainfall occurring between 6/27/83 and 7/8/83. This figure may seem low. However, as discussed in a previous section, some of the rains were relatively light (less than 0.5 inches, spread over a number of hours) and generated little runoff; the area is marked by high infiltration, and major runoff events exceed the capacity of some sinkholes to swallow all the runoff reaching them. Also, some streamflow into sinkholes is lumped with infiltration recharge, especially during recession, as previously discussed. The analytical separation may be checked using an approach that is essentially similar to that used for the chemical separation, discussed for the snowmelt events.

Total, conduit-flow, and diffuse-flow discharges are taken from the hydrograph and the analytical separation. The concentration of a given chemical parameter, which is known for the total discharge, is estimated for one (or both) of the two flow components. The concentration of this parameter in the second flow component is then calculated. This was done using specific con-

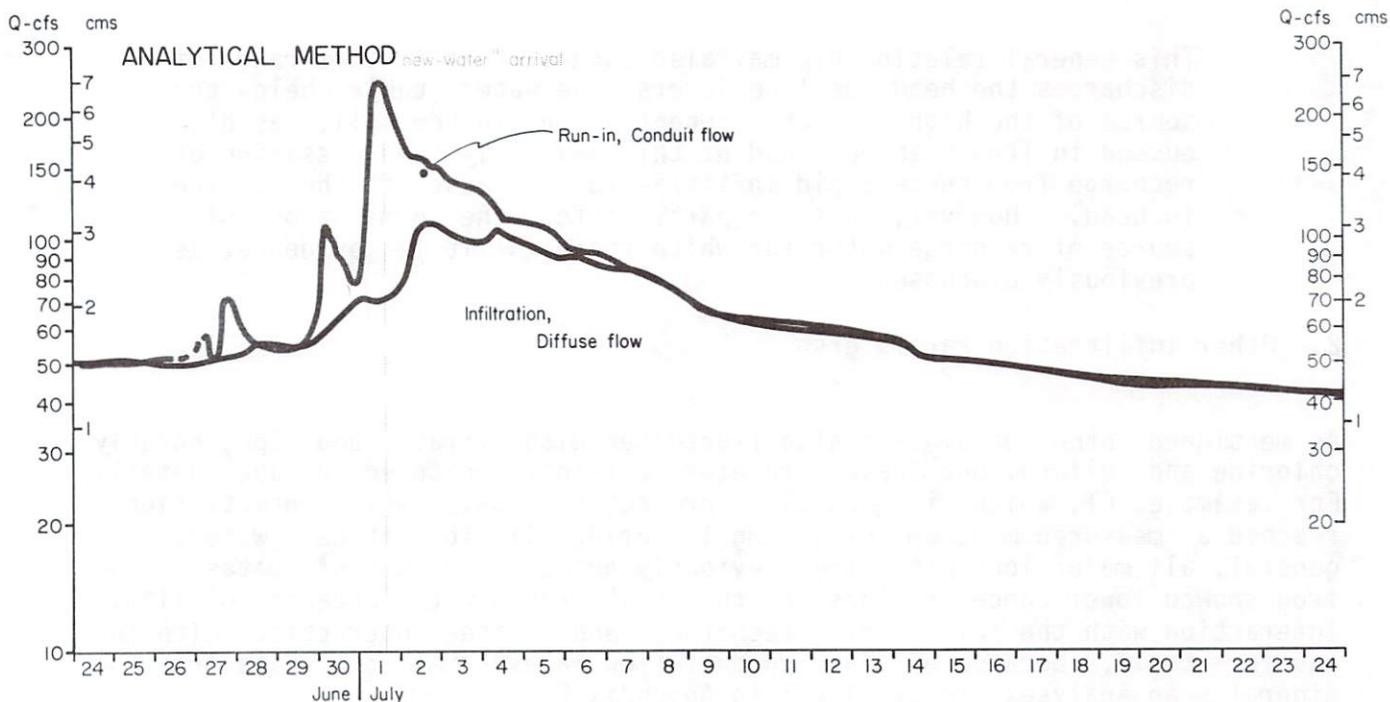


Figure 32. Analytical hydrograph separation of the mid-summer event.

ductance and atrazine. A specific conductance of $700 \mu\text{mhos}/\text{cm}^2$ was estimated for the diffuse-flow component. At maximum dilution, a conduit-flow component conductance of $440 \mu\text{mho}/\text{cm}^2$ is indicated. During peak discharge at surface-water site Boog-U, just upstream from where the stream is swallowed by sink-holes, a specific conductance of $180 \mu\text{mhos}/\text{cm}^2$ was measured during runoff. Specific conductance will increase during subsurface flow, principally through dissolution of the calcite and dolomite comprising the Galena aquifer. The magnitude of this increase is uncertain. Bassett (1974) noted average increases in hardness (calcium plus magnesium concentrations) of about 40%, under flow rates of 5.5 miles/day or less, in conduit-flow groundwater within the karst areas of southern Indiana. Data from Jacobson and Langmuir (1970) indicate that specific conductance roughly triples in sinking stream-spring systems in Pennsylvania, over a 9000 foot (2700 m) flow path and 1000 feet/day (300 m/day) flow velocities. If the analytical method is giving a realistic two component separation, the specific conductance of surfacewater runoff increases 2-2.5 times during peak subsurface conduit-flow. While this increase seems reasonable, it does not provide the best check on the validity of the separation.

Atrazine concentrations yield a better check on the hydrograph separation. Atrazine has no natural subsurface source, although some atrazine is likely attached to sediments within the conduit system. Background concentration during diffuse-flow dominated periods are about $0.2 \mu\text{g}/\text{l}$. This value was used as the atrazine concentration in the diffuse-flow component. (A value of 0.4

$\mu\text{g/l}$ was also used, as this was the atrazine concentration in diffuse-flow periods after the event; calculated conduit-flow values are only 0.1 -0.2 $\mu\text{g/l}$ less when this higher value is used.) From these calculations, atrazine concentrations ranging from 5.8 to 8.7 $\mu\text{g/l}$ are indicated for the conduit-flow component, when discharge is above 150 cfs. Measured atrazine concentration at Boog-U was 6.6 $\mu\text{g/l}$ during peak discharge, and atrazine levels in mid-summer surface runoff are generally between 5-10 $\mu\text{g/l}$. As noted in previous sections, closely-spaced sampling delineated two peaks in atrazine concentration in Big Spring discharge. The first (1800 hours, 7/1/83), 4.7 $\mu\text{g/l}$, has a calculated conduit-flow atrazine concentration of 6.7 $\mu\text{g/l}$, virtually matching the measured value at Boog-U. The second peak (0030 hours, 7/2/83), 5.1 $\mu\text{g/l}$, was associated with the highest calculated atrazine level, 8.7 $\mu\text{g/l}$. The generally good agreement between measured and calculated atrazine values supports the overall validity of the hydrograph separation shown in figure 32.

Specific conductance measurements were also used to separate the hydrograph (figure 33). Assumed flow component concentrations were 700 $\mu\text{mhos/cm}^2$ in baseflow and 400 $\mu\text{mhos/cm}^2$ in conduit flow. The conductivity based separation indicates that the diffuse-flow component delivered 87% of the total discharge, compared with the 77% indicated by the analytical separation. The effect of displacement water is clearly seen in the separation, as the diffuse-flow component dominates the rising limb of the 7/1 discharge event and then drops dramatically at the new-water arrival. Compared to the analytical separation, the conductivity-based method suggests an earlier return to total diffuse-flow conditions. Conductivity returns to 700 $\mu\text{mhos/cm}^2$ by 0930 hours on 7/3/81, at a discharge of about 140 cfs (4.0 cms). By 7/8/83, conductivity was 730 $\mu\text{mhos/cm}^2$, and was at 780 $\mu\text{mhos/cm}^2$ by the end of July. Processes other than simple dilution were affecting the diffuse-flow component conductivity. Also, using a single value for the conduit-flow component involves problems. On small streams such as those in the Big Spring basin, shallow-groundwater flow (interflow and direct tile-drainage) is often an important contributor to streamflow, and may cause significant increases in dissolved constituents, and the conductivity as the flood wave passes. The separation generated by the analytical method, checked with atrazine-concentrations (which acts as a "tracer" of runoff water) is considered the more valid of the two separations, and points out the usefulness of combining classic analytical methods with chemical analyses of proper parameters. Both methods reveal different features though and are worthy analytical tools; the SpC separation clearly shows the displacement water but returns to base-flow too quickly as indicated by other parameters. The small difference (10%) between the methods, however, provides a perspective on the validity of the numerical estimates of the flow parameters.

Chemical Delivery by Flow Components

The hydrograph separation (figure 32) may be used to estimate the chemical loads discharged by the infiltration-recharge, diffuse-flow component and the runoff-recharge, conduit-flow component. This was done in two ways, using a weighted and unweighted concentration for the chemicals of concern, nitrate-N and atrazine. For the unweighted method, the measured concentrations are simply assigned to the water volumes indicated by the analytical hydrograph

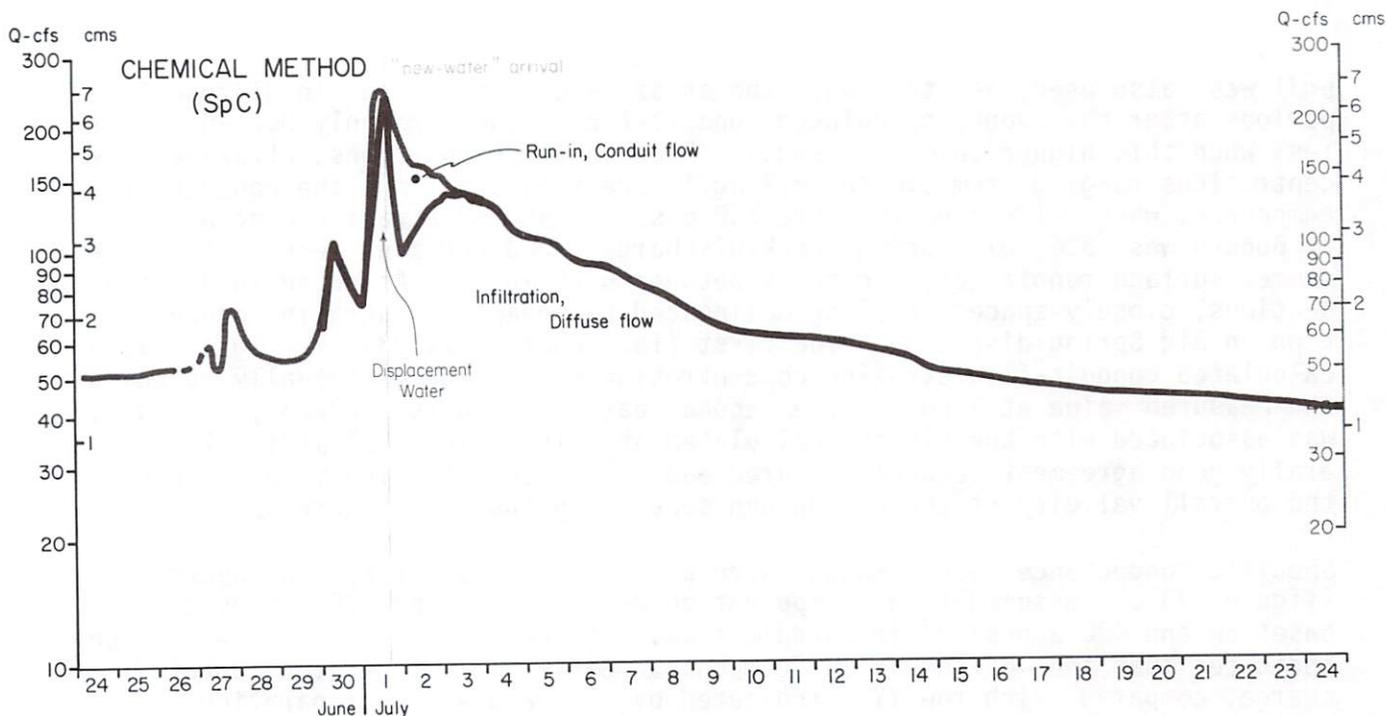


Figure 33. Hydrograph separation of the mid-summer event using specific conductance.

separation. Weighted loads are derived by assigning estimated chemical concentrations to one (or both) of the flow-components (derived from the detailed monitoring). For nitrate, diffuse-flow component concentrations of 75 and 80 mg/l were used; the diffuse-flow atrazine concentration was considered to be 0.4 $\mu\text{g/l}$. As noted in the previous discussion these values are very realistic in relation to the observed values. Thus, the "weighted" analyses are considered to be more realistic, but should be compared with the unweighted values for perspective. Results of the calculations are given in Table 14. Even the unweighted values show that the diffuse-flow component is enriched in nitrate, and the conduit-flow component is enriched in atrazine. Weighted values indicated that diffuse-flow (77% of total discharge) delivers 87% (76,930 lbs, 34,890 kg) of the nitrate-N, while conduit flow (23% of the total discharge) delivers 80% (7.2 lbs, 3.53 kg) of the atrazine.

Groundwater discharge for the period 6/30/83-7/11/83 was 2,394 acre-feet (2.95 million cm), more than was discharged during any one of the low-flow months of August, September, or October. This volume is about 6% of the total discharge from the Galena aquifer for the Turkey River for the water-year (12 days is about 3.3% of the water year). The conduit-flow discharge during this period, 560 acre-feet (0.69 million cm), was about 12.5% of the annual total. During this period, 88,420 lbs (40,100 kg) of nitrate-N was discharged; more than was discharged during most low-flow months. This N-load represents 7.7% of the nitrate-N discharged to the Turkey River during the water-year. Total atrazine discharge was 9.1 lbs (4.4 kg), 29% of the total for the water-year.

Table 14. Summary of Big Spring analytical hydrograph separation data for the 6/30-7/11/83 events.

A. Water Discharge	Millions Cu Ft	Millions Liters
Total	104.3	2,955
("Infiltration") Base Flow - 77%	80.3	2,275
(SpC Separation - 87%)		
("Runin") Peak-Conduit Flow - 23%	24.0	680
(SpC Separation - 13%)		
B. Nitrate-N Discharge	Pounds	Kilograms
Total	88,420	40,100
"Unweighted"		
Base Flow - 79%	69,850	31,680
Conduit Flow - 21%	18,570	8,420
"Weighted"		
Base Flow - 87%	76,930	34,890
Conduit Flow - 13%	11,490	5,210
C. Atrazine Discharge	Pounds	Kilograms
Total	9.1	4.41
"Unweighted"		
Base Flow - 60%	5.8	2.64
Conduit Flow - 40%	3.3	1.77
"Weighted"		
Base Flow - 20%	1.9	0.88
Conduit Flow - 80%	7.2	3.53

These figures show the importance of the contributions that large storm events can make to annual chemical losses. Particularly, they demonstrate the important contribution of major runoff-recharge events to pesticide losses.

Tile-Line Monitoring: A Proxy of Shallow Groundwater Quality Responses

The parallel responses in water-quality changes over time (see figure 6) between tile-line discharge water and the groundwater (as shown by water-quality

at Big Spring or in well-networks), illustrate, as previously discussed (see also Hallberg et al., 1983; Libra et al., 1984), that these data can be used as a proxy indicator of the behavior in the shallow soil-groundwater system. This is true not only for the changes in nitrates (as in figure 6), but also, as discussed by Hallberg and others (1983) and Libra and others (1984), the species and concentrations of pesticides in tile-line discharge water are indicative of the concentrations of pesticides routinely found in the deeper groundwater. Tile lines are, in essence, long, shallow, horizontal collector wells. Although tile lines may enhance the losses (and hence concentrations) of nitrate-N, because of accelerating drainage flow rates (Baker and Johnson, 1977), in areas of high infiltration the quality of the tile-line water closely approximates that found in shallow groundwater which is used for drinking water (Libra et al., 1984; Hallberg et al., 1983).

There are three important proxy observations that can be made from the monitoring of the tile lines: 1. the inter-relationships among chemical application-land management, tile-drainage water quality, and groundwater quality; 2. the mechanisms of soil-water, groundwater and solute movement; and 3. the timing of the response of the soil-water, solute system to recharge events. First, as previously discussed, the long-term seasonal fluctuations in nitrate concentration in the tile drainage water (draining land in continuous, fertilized corn) directly parallels those fluctuations in the groundwater system, showing that the same processes of water movement and leaching of nitrate that affect the tile drainage carry through the hydrologic system into the bedrock aquifers in a region such as this. The importance of these observations is that many studies have shown that the concentration and amount of nitrate-N discharged in the tile-water is directly related to the rate of N-fertilization (e.g., Baker, and Johnson, 1977; Gast et al., 1978; Baker and Laflen, 1983; Kanwar et al., 1983; Nelson and Randall, 1983). Such data show the link among agricultural-management practices, tile-drainage water quality, and groundwater quality. Second, the observations from the tile-drainage water provide insights into the mechanisms of soil-water, shallow-groundwater and solute movement. The movement of soil-water and contained solutes takes place by two processes (and various combinations): 1) displacement flow, or mass-flux, where, in a saturated or near-saturated state, the soil-water and solutes are displaced downward through the soil matrix by the addition of additional water (and thus, additional head) from above; and 2. by water (and solute) flow-through-macropores, which may take place under various conditions of soil moisture, where water moves more rapidly downward through large pores and physical discontinuities (root tubules, animal burrows, frost or shrinkage cracks, or cracks or voids between soil-structural units) in the soil. Flow-through-macropores is now thought to be far more important than previously recognized (Thomas and Phillips, 1979; Quisenberry and Phillips, 1976; Shufford et al., 1977; Baker and Johnson, 1981; Simpson and Cunningham, 1982; Pettyjohn, 1982; McKeague et al., 1982; Megahan and Clayton, 1983; Germann et al., 1984). These two processes may have very different effects on the quality of water discharged from the tile line (e.g., previous citations). The third important observation, deals with the timing of the response to rainfall-recharge events. As noted previously, with widespread climatic events (rainfall or snowmelt) tile-drainage in widely separated parts of the Big Spring basin responds simultaneously.

Another intriguing factor of the observations on the tile-drainage water is that the soil-tile line system is a direct, small-scale analogy of the karst-

groundwater system. Both systems may be described, in general, as three component system (e.g., Libra et al., 1984). The matrix of the soil, (and the aquifer) is marked by microporosity and relatively low interstitial hydraulic conductivity. The tile-lines in the soil are analagous to the large conduits in the karst-carbonate aquifer flow system; they mark a zone of very rapid groundwater movement which draws down the potentiometric surface and induces water flow towards and into them. The third component is intermediate between these end members--grading from one to the other--and includes the zones of macropores with intermediate porosities and conductivities. This "intermediate" condition is likely dominant on an areal basis. The movement of water, and the quality of water, transmitted through the soil may differ depending on what conditions dominate at a given time.

It is important to recognize that much of the macroporosity will function at all times, over a wide range of conditions (though macropores related to frost or dessication cracking may not persist). When the soil is relatively dry (or in the aquifer with a low potentiometric surface during base flow) and macropores are open to the surface, precipitation or runoff water will be able to directly percolate down into the soil. This water will have very low concentrations of mobile soluble constituents such as nitrate, because of the short "residence time" and limited interaction with the soil. This water will only mobilize small amounts of nitrate and the flow of this water into the tile line will cause nitrate concentrations to decrease relative to base flow conditions. However, such flow may transmit small amounts of nitrate deep into the subsoil (e.g., Thomas and Phillips, 1979).

Tillage will disrupt macropores in the "tilled" or plow-zone, and thus for some time after tillage macropores may not extend to the surface. This does not preclude macropore flow; deep percolation through macropores still occurs, though to a lesser extent than in an undisturbed soil (Quisenberry and Phillips, 1978; Thomas and Phillips, 1979). Under such conditions the soil-moisture in the plow-zone will increase until the potential is great enough for water to enter the macropores. Then the water will move down the macropores under gravitational potential, even if the soil is below field capacity moisture content (Quisenberry and Phillips, 1976; Aubertin, 1971). If, as is often the case (e.g., Baker et al. 1975; Gast et al., 1978; Baker and Johnson, 1981), there is a large amount of available nitrate in the plow zone, this nitrate will be mobilized in the soil water and high concentrations of nitrate may be transmitted down the macropores, deep into the subsoil, or into an aquifer below (e.g., Thomas and Phillips, 1979). If the subsoil matrix is not saturated, water and nitrate (or other solutes) from the macropores will enter into the matrix by direct infiltration as well as diffusion.

Under saturated conditions the macropores will still function as avenues of rapid water and solute transport, though their effects will be less obvious. Because the macropores transmit water much more quickly than the matrix they will, in effect, "drawdown" the zone of saturation, increasing potential, and cause water from the saturated matrix to flow into the macropores. Thus, the macropores will enable water and solutes, such as nitrate, to drain to depth (to a tile-line, or to an aquifer, etc.) much more rapidly than they would through the matrix itself. Thus, macropores may play an important role in both the recharge of water into the soil, and the redistribution of solutes in the soil, as well as the discharge through the soil (under saturated or unsaturated conditions). The downward leaching of mobile solutes, such as ni-

trate will not be as thorough under macropore flow as with saturated-displacement flow, however.

These effects have direct analogies in the karst-carbonate aquifers where "macro-fractures" serve a similar capacity (see Libra et al., 1984). If the macro-fractures are directly open to the surface, or if they have a soil mantle covering them similar differences in nitrate movement will occur as described above.

The monitoring of the quality of tile-drainage water provides some examples of these mechanisms. As noted, during snowmelt the nitrate concentrations decline sharply in all parts of the hydrologic system--in the groundwater in wells or at Big Spring, in surfacewaters, and in tile lines (see figures 6-8, and Hallberg et al., 1983). As snowmelt began the tile drainage discharge increased (as noted in the field and through 'stage' measurements of the water-level in the tiles) and nitrate concentrations dropped sharply from values of 70-80 mg/l to 30-40 mg/l. During this time the soil matrix was still frozen and little or no matrix-displacement flow could occur. Also as the soil began to thaw and tile discharges remained high, the nitrate concentration abruptly rose back to near their pre-snowmelt values, and then more slowly climbed to higher levels even as tile-discharge fluctuated and declined. Even if we ignore the fact that the soil matrix was frozen, such behavior could not occur simply through displacement flow. Changes in nitrate concentrations in tile-drainage water may be related to the depth where nitrate is stored in the soil profile at a given time (Baker et al., 1975). However, as noted previously, high concentrations of nitrate can almost always be found in the upper portions of the soil profile (particularly in fertilized continuous corn areas, such as discussed here) and soil sampling (described in the section below on soil core analyses) in the Big Spring basin in the late-fall and early-winter of 1982 and 1983 show that to be the case here as well. Also, if the decrease in nitrate concentrations was caused by low concentrations of nitrate in the upper portions of the soil profile (which would be involved as the top of the zone of saturation rose to increase tile drainage) then nitrate concentrations would not rise sharply as the soil matrix thawed out nor as further rainfall infiltration events took place.

The reduction in nitrate concentrations is caused by recharge of snowmelt water down macropores (likely enhanced by frost-cracking) which dilutes the nitrate concentrations, in the same manner it does in surfacewaters and the runin component of the groundwater at Big Spring.

Unfortunately, the tile-drainage waters were not sampled in detail during the April, 1983 nitrate "plateau" events. The detailed observations during the June-July events, however, provide a sharp contrast with the snowmelt period (figures 6 and 19). As described, previous to the June-July events conditions had been dry and the first rains, even though considerable, did not generate much runoff. Unfortunately, by the initial sampling of the tile-drainage waters their discharge had already increased and nitrate-concentrations also increased sharply from values of 70-90 mg/l to 110-140 mg/l. With over 7 inches (180 mm) of rain that fell soils did become saturated (from field observations). Combined processes of matrix-displacement flow and macropore flow mobilized large amounts of nitrate-N from the upper portions of the soil profile, displacing them to depth, to tile-drainage water, to the aquifer, or to depth in the subsoil. After these events the weather was quite dry (figure

1) and as the water table dropped nitrate concentrations in the tile water also dropped sharply, returning to their former values by late July (figure 6). As hot, dry weather and recession continued, the nitrate concentrations further declined to less than their spring and early summer values.

Another rainfall-discharge event was monitored in some detail in early October, 1983 (the beginning of water-year 1984). This event again followed rather dry antecedent conditions and generated an interesting, mixed response from the tile-lines (figure 34).

Gentle rain began to fall about 0100 hours on 11 October, and continued until about 0100 hours on 12 October. About 2 inches (50 mm) of rain fell. The tiles had been sampled on 3 October, and detailed sampling began at 0700, 11 October and continued at about 3-4 hour intervals through 13 October.

Figure 34 shows some of the pertinent data: 1. discharge and nitrate concentrations at Big Spring; nitrate-concentrations from: 2. tile-line L22T (site 109, figure 3), which drains an area of alluvial soils along Silver Creek which is cropped in continuous corn; 3. Silver Creek, L23S (site 110, figure 3) just downstream from L22T; 4. several sites from the Bugenhagen basin (figure 3 and 4), BTL-1(UW), a tile line which drains an area of sloping loess soils and a small upland drainageway in continuous corn; 5. Boog-U surface-water site near where BTL-1(UW) discharges into it; 6. BTL-2(D) a tile line which drains a fertilized pasture, downstream from the BTL-1, Boog-U sites and drains soils similar to BTL-1; and 7. Boog-D a station on the same stream as Boog-U, but downstream near BTL-2.

By 1000 hours, 10/11/83, the nitrate concentrations in L22T and BTL-1 had dropped slightly, perhaps indicating macropore-recharge and dilution. No runoff had begun yet and surfacewater nitrate concentrations remained stable. By 1200 hours some runoff had begun in headwater areas and Boog-U nitrate concentrations quickly fell below detectable levels (<5 mg/l). By 1500 hours runoff had peaked and all the surfacewater sites showed sharp reductions in nitrate. In this short time the tile-line nitrate concentrations changed abruptly and simultaneously, but differed in direction.

After an initial small drop in concentration, the nitrate concentration rose sharply from 57 to 71 mg/l in L22T, draining the alluvial-bottomland soils. In contrast, while L22T rose BTL-1 simultaneously decreased from 61 to 22 mg/l. BTL-2, draining the pasture showed very little change, declining only 1-2 mg/l, but it also changed synchronously.

During the peak tile flow L22T remained high, increasing to 73 mg/l, while BTL-1 increased to 34 mg/l by 0030 hours on 10/12. Surfacewater-runoff recession began earlier (by 2200 hours 10/11) and by 0030 surfacewater nitrate concentrations had begun to rise.

Subsequently tile-drainage discharge also declined. As it did so the nitrate concentrations also declined slightly at L22T to about 70 mg/l and then on 10/13 (figure 34) rose to higher levels yet at 75 mg/l. Nitrate at BTL-1 rose sharply during recession reaching 60 mg/l by 2100 hours on 10/12. As with L22T, nitrates at BTL-1 then rose slowly reaching 67 mg/l on 10/13 and then gradually rose to 74 mg/l the following week (figure 6). As runoff ceased, surfacewater discharge recessed and by 1200 hours on 10/12 streamflow

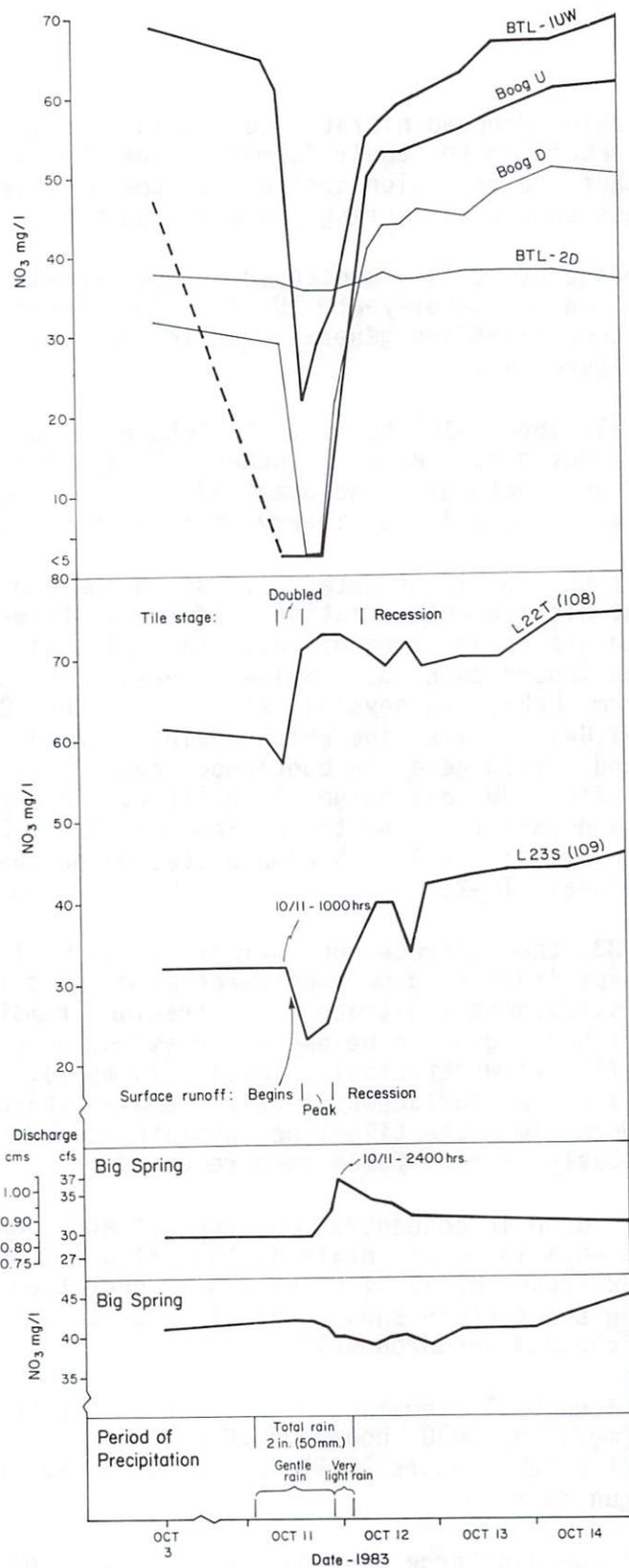


Figure 34. Nitrate concentrations and discharge notes from October event for Big Spring and various tile lines and surfacewater sites.

was comprised solely of shallow groundwater flow-interflow, tile-drainage, and bank-storage return flow. By 10/12 nitrate concentrations in the streams ;had risen to levels 15 to 20 mg/l higher than they were before this interval.

On the east side of the basin where, in the high-infiltration area where the piezometric surface in the aquifer is very deep beneath the land surface, no runoff or tile-drainage was initiated by this rainfall. Thus, only a very small response was noted at Big Spring (figure 34). Discharge rose slightly, but rapidly, from about 30 cfs (0.85 cms) at 1700 hours, 10/11, to 37 cfs (1.0 cms) at 2400 hours. Discharge peaked about 12-14 hours after runoff-runin began. Nitrate concentrations decreased slightly from 42 mg/l and fluctuated around 39-40 mg/l until 10/13. On 10/14 nitrates began to rise gradually, about 36 to 40 hours after when runoff stopped and surfacewater nitrate concentrations began to rise more sharply. After this, additional rains the following week caused a sharper rise in nitrate concentrations (see figure 6). These response times are similar to those described previously. The observation suggest that another reason for the rapid response time of such small events may be that only the western sinkholes receive runin with such small events, and as noted the travel time from this part of the basin is less than from the east side.

The different responses in the three different tile lines, under different soil and/or crop conditions, illustrate the range of processes and responses possible in the shallow soil-groundwater system. It also points out the complexity of chemical responses that may occur under dry antecedant conditions in late-summer early-fall seasons. Although the response of the tile-drainage to the rainfall was rapid and synchronous, the processes affecting them, and hence the nitrate concentration changes were very different.

Discharge from tile-line BTL-1 was dominated by macropore flow, dilute in nitrate, causing the sharp decline in nitrate concomitant with the rise in discharge. Even while discharge remained high nitrate concentrations increased, suggesting that some matrix-displacement water with higher nitrate concentrations began discharging. Upon recession nitrates rose more sharply and reached levels higher than before the event began. This suggests that additional nitrate was displaced lower in the soil, so that as discharge, and hence the water table, fell to lower levels more nitrate was discharged.

At L22-T the situation was different. The initial, albeit small, drop in nitrate concentrations also suggests that macropore flow initiated the increase in discharge. However, nitrate concentrations abruptly reversed trend and rose sharply as discharge continued to increase. This suggests that, possibly in these alluvial soils, infiltration of the rain water was more effective at saturating the soil matrix and displacing water, with high concentrations of nitrate, through the soil profile.

Tile-line BTL-2, in the pasture area showed the same discharge response but almost no change in nitrate concentration. This may be related to two factors. This pasture area is lightly fertilized every other year (or so) but has not been cropped to corn, with heavy fertilization for over 5 years. Thus, nitrate concentrations are (as obvious from the discharge data) much lower than in the continuous corn areas, and is likely more uniformly distributed (in terms of comparative concentrations) in the upper few feet of the soil. Second, although the soils will have macropores related to plant roots

and soil structure, with the more dense plant cover and no exposed soil (as between the corn rows) there is not likely to be as many desiccation-crack macropores at the soil surface as at BTL-1. The very minor dilution that occurred may reflect minor macropore flow mixed with matrix-infiltration which caused a head increase and displacement of similar nitrate concentration water.

SUSPENDED SEDIMENT, ORGANIC-N, AND AMMONIUM-N: PROPERTIES AND ESTIMATES OF ANNUAL DISCHARGE

As discussed, suspended sediment, organic-N, and ammonium-N were monitored intermittently at Big Spring during the water-year. From these data, and the general relationships discussed for discharge events of various magnitudes, some estimates of the total, annual discharge of these parameters in groundwater can be made.

Suspended Sediment

The suspended sediment load during groundwater base-flow at Big Spring is low, averaging about 440-480 lbs/day (200-220 kg/day). As discussed for the late June-early July events, during peak, conduit-flow events suspended sediment loads are very high, similar to surfacewater values, and achieve discharge rates of 192,000 lbs/hour (87,000 kg/hour). The total discharge of suspended sediment at Big Spring for water-year 1983 is estimated to be approximately 7,012,000 lbs or 3,506 tons (3,180,200 kg). Approximately 98% of this sediment was discharged during conduit, peak-flow discharge events. This is one of the principle reasons that these events create serious problems for water management at the ICC Fish Hatchery. If this mass of sediment is proportioned back over the sinkhole basins, for perspective (and noting the prior discussion of the shortcomings of the assumptions involved), this would average about 0.5 tons/acre/water-year 1983.

As also noted in prior discussion, the suspended sediment load varies in character over time, both in terms of particle-size and the amount of organic matter that may be associated with the sediment. Table 15 summarizes the data from analyses of the suspended sediment samples (sampled from sediment traps installed at Big Spring). A few generalizations can be made. First, early spring and snowmelt samples tend to be more coarse (i.e., -contain more sand, and more coarse sand) than samples from later in the year. These spring samples tend to have less organic debris associated with them, also. Second, there is very little nitrate associated with the sediment, as would be expected. Third, both dieldrin and atrazine occur attached to the particulates (clay particles) or organic matter, in varying concentrations. When detected, Dieldrin associated with the sediment ranged from 0.60 to 8.0 $\mu\text{g}/\text{kg}$, and atrazine ranged from 2.6 to 9.2 $\mu\text{g}/\text{kg}$. These two pesticides have also been detected associated with the suspended sediment in streams draining into sinkholes, as has the insecticide Furadan (carbofuran), in concentrations ranging from 0.6 to 1.1 $\mu\text{g}/\text{kg}$ dieldrin, 1.1-2.6 $\mu\text{g}/\text{kg}$ atrazine, and 1.9-3.5 $\mu\text{g}/\text{kg}$ Furadan.

Mineralogical analysis of the sediments has shown that the coarse fraction (sand-size particles) is dominated by material derived from the rock of the Galena aquifer, while the fine (clay) fraction is a typical mix of materials derived from the soils and Quaternary deposits in the basin. The sand fraction is typically dominated by abraded dolomite rhombs, derived from mechanical erosion of the Galena aquifer. The clay mineralogy (see Hallberg et al., 1978 for methods) from these samples ranged from 42-59% for expandable clay minerals (smectite), 25-38% for illite, and 17-20% for kaolinite and chlorite. This covers the typical range for different Quaternary deposits in the region (see Hallberg, 1980).

Organic-N, Ammonium-N

Organic-N and ammonium-N are other compounds which contribute to the total nitrogen loss from the basin. As noted their presence in groundwater coincides with surfacewater runoff, conduit-flow events, and their concentration vary, rather directly, with the suspended sediment concentration. Ammonium-N has never been detected in groundwater during base-flow periods or even moderate magnitude conduit-flow events. Similarly, organic-N is usually not detectable during base-flow but does appear in some concentration during most peak-discharge events. Thus, these constituents are associated with the runoff, conduit-flow components.

For water-year 1983 the amount of organic-N discharged in groundwater is estimated at approximately 19,300 lbs-N (8,750 kg) and the amount of ammonium-N at 1,080 lbs-N (490 kg). This is a negligible amount of nitrogen compared to the mass of nitrate-N discharged (see Table 8); together organic and ammonium-N equal only 1.5% of the nitrate-N discharged from the basin in groundwater or about 0.7% of the total (surfacewater and groundwater) nitrate-N discharged. In surfacewater organic-N and ammonium-N concentrations are generally greater and more persistent. Surfacewater contributions of these N-species were not monitored in detail to sufficiently warrant a quantitative estimate, but it is apparent they would likely add 5-10% additional to the total N lost from the basin.

NITRATE AND PESTICIDE ANALYSES FROM SOIL CORES

During the course of the Big Spring study numerous soil cores have been collected to examine the the nature of the soils and the thickness and stratigraphy of the Quaternary deposits in the basin. A number of sites were cored in October and November in 1982 and 1983, after corn harvest. At 21 of these sites, under different landuse, soil samples were collected for laboratory analysis for nitrate-N and pesticides which may be stored in the contained soil water.

Soil cores were taken using a trailer-mounted Giddings hydraulic soil-coring machine. Either two or three inch (5 or 7.6 cm) diameter cores were taken at each site. The cores ranged from a few feet to 35 feet (1-11 m) in depth

Table 15. Analyses of suspended sediment samples from Big Spring.

DATE COLLECTED	Sand	PARTICLE-SIZE			PESTICIDES	NITRATE	ORGANIC MATTER*
		Coarse Silt %	Fine Silt	Clay			
					µg/kg	mg/kg	
<u>1981</u>							
10/27					N.D.		
11/10					N.D.		
<u>1982</u>							
3/18 ²	36.3	44.7	9.5	9.4		0.2	
3/22 ²					0.65 (Dieldrin)	0.4	
9/6	40.3	34.3	17.7	7.7			
9/22					8.0-Dieldrin		0*
11/3					3.6-Dieldrin 5.1-atrazine		
11/30 ²	24.8	35.4	23.1	16.7	1.1-Dieldrin 5.0-atrazine	0.6	0
12/8 ²	26.3	47.4	14.5	11.8			
<u>1983</u>							
2/22 ²	49.3	32.8	11.8	6.1	9.2-atrazine		
5/4 ²					1.1-Dieldrin		
7/2 ²	21.8	20.7	38.6	18.9	2.6-atrazine 0.6-Dieldrin		0 ¹

*0 - Abundant, decomposed organic matter in sample.

¹ - Organic matter dominates sample; with numerous water worn woody fragments, pieces of corn cobs.

² - Sample related to conduit peak-flow event. Other samples are integral of long sample collection period.

(dependent on the depth to bedrock). The soils and geologic materials were described and samples were collected from selected horizons.

All cores were collected from relatively level surfaces (A or B slopes) in various landscape positions. All sites were a minimum of 25 feet (7.5 m) in from fence rows or end rows. In corn fields all coring was done in inter-row areas. For N-balance studies using soil cores it is common practice to take and analyze duplicate (or multiple) soil cores from each plot because of the variation in nitrate content, particularly in the upper few feet (1 m) of the soil profile (e.g., Cameron et al., 1979). For this study, duplicates were run only from a few sites. The primary purpose of these soil analyses was to gather some background information on the concentrations of nitrate and pesticides at depth (as well as near the surface) under different landuse-land management. Limitations of funding precluded running duplicates of cores that were analyzed to depths of 20 feet (6 m). However, the variability apparent from the duplicates that were run, was not great enough to affect the comparison of the marked differences between different landuse areas.

The soil sample analyses were done by UHL. The soils were analyzed for nitrate using the Army Corps of Engineer's elutriate method (U.S. Army Eng., Waterways Exp. Station, 1976, Misc. Paper D-76-17, "Ecological evaluation of proposed discharge of dredged or fill material into navigable waters."). Moisture contents of the soils were determined gravimetrically. The nitrate-N was extracted with a 1:4 ratio of sample to demineralized water with at least one-half hour of agitation. The extracted water was clarified, decanted and analyzed using standard Cd-reduction technique; therefore the concentration data include $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$. More detailed analysis show almost no $\text{NO}_2\text{-N}$ was present. According to some studies this procedure may not extract all the $\text{NO}_3\text{-N}$ (see Lindau and Spalding, 1984).

The soil samples were analyzed for pesticide residues following EPA methods (U.S.E.P.A., June 1980, Manual for the analysis of pesticides in humans and environmental samples, EPA-600/8-800-083, section 11). In brief, a soil sample at about 10% moisture content was mixed with (1:1) sodium sulphate and ground. Pesticides are extracted using a solvent flux of acetone and hexane. The pesticide concentrations are routinely determined by gas chromatography.

All results are expressed in terms of the dry weight of the sample (e.g., mg/or $\mu\text{g}/\text{kg}$). For discussion the nitrate-N data has been converted into kg/ha equivalents, using the concentration and the bulk density of the soil materials. These data have been summarized by depth in 20 cm (8 inch) increments in the surface soil horizons, and in 50 cm (20 in) increments with depth. The various data are tabulated in Appendix 3.

Soil Nitrates

The data for nitrate-N in the soil profiles is summarized in Table 16 and figures 35 and 36. Figure 35 shows graphs of the amount of $\text{NO}_3\text{-N}/\text{ha}$ per 50 cm (20 in) increment of depth in the soil profile for selected sites. In essence this shows the normalized concentration of $\text{NO}_3\text{-N}$ with depth in the various profiles. Figure 36 shows the cumulative amount of $\text{NO}_3\text{-N}/\text{ha}$, with depth, for

the same sites. Table 16 summarizes the high and low range for the concentrations and cumulative $\text{NO}_3\text{-N}$, under different landuse.

Figure 35A shows the distribution of $\text{NO}_3\text{-N}$ beneath long term forested areas (in forest the past 40 to 50 years). The highest concentrations of $\text{NO}_3\text{-N}$ are found in the top 50 cm (20 in); this is related to natural mineralization of organic-N in the O/E horizons of these soils. The concentrations decline and are stable at low values with depth. Figure 35B shows plots from an area of second-year alfalfa hay, in a low-chemical fertilization rotation with corn (less than 80 lbs-N/ac, 90 kg-N/ha, applied in corn years), a pasture, and a heavily-grazed, lightly-fertilized pasture. These data are similar to the forested areas, but exhibit slightly higher $\text{NO}_3\text{-N}$ with depth (below 50 cm). This is more clearly noted in figure 36A and B which show the cumulative data. These similarities are supported by other studies which have shown that runoff and drainage water quality is similar between forested areas and unimproved pasture (e.g. Owens et al., 1983a) and that increased nitrate losses from pasture areas generally are related to fertilization of pastures not animal wastes (Owens et al., 1983b, 1984). Together the $\text{NO}_3\text{-N}$ data from the forested-pasture-meadow rotation areas form a background to compare to other sites.

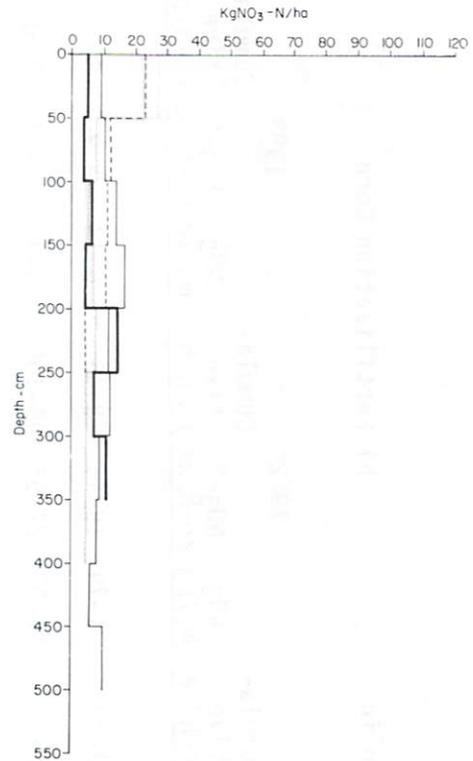
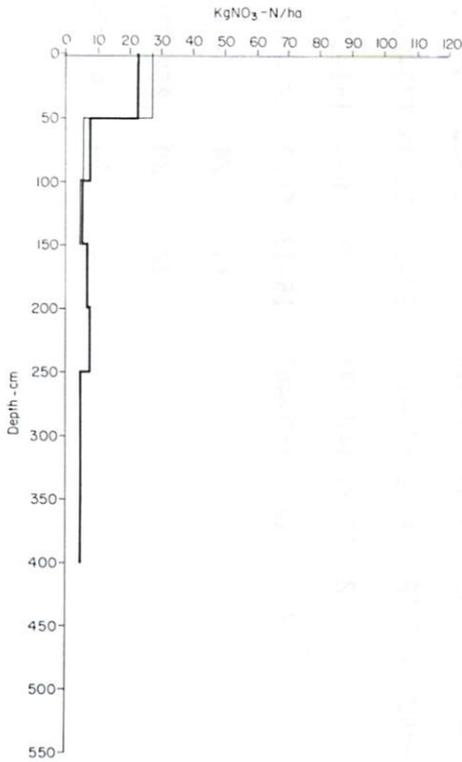
Figures 35C and 36C show a plot of $\text{NO}_3\text{-N}$ with depth for an area in first-year high-chemical fertilization (150 lbs-N/ac, 165 kg-N/ha or greater) corn. The area had been forested until 1981-1982 when it was cleared, and then planted to corn. Note that the $\text{NO}_3\text{-N}$ in the top 50 cm is nearly double that of the background data, but with depth the amount of $\text{NO}_3\text{-N}$ is very similar to the forested-pasture areas. Figure 35D and 36D shows the $\text{NO}_3\text{-N}$ distribution after the second year of high-fertilization corn, after an alfalfa rotation; after two years of fertilization this site shows $\text{NO}_3\text{-N}$ accumulations greater than the first year corn in the 0-50 cm increment, and above the background data to depths of 2.0 m (about 6 feet).

One core was taken to evaluate the concern with small, but numerous, feedlots in the basin as a source of nitrate in the groundwater. Figure 35E shows the nitrate distribution with depth from a long-term active, earthen cattle feedlot (about 0.6 acres in size; 0.2 ha). As shown on figure 35E, nitrate-N levels (average of duplicate samples) are quite high in the first 50 cm; this increment includes the manure layer and the uppermost mineral-soil beneath the manure. Below 50 cm, however, $\text{NO}_3\text{-N}$ amounts return to background level, and there is no obvious indication of a nitrate buildup or leaching beneath the feedlot. Although excessive manure applications to tilled land can result in nitrate leaching (e.g., Cooper et al., 1984; Adriano et al., 1971) various studies show that little leaching occurs from active earthen feedlots or earthen manure-storage structures. These studies (Ritter et al., 1980; Ellis et al., 1975; Oliver et al., 1974) suggest that while such feedlots or storage structures are actively used that: 1. the soil becomes sealed by the organic matrix of the manure pack and compaction by the animals, physically preventing leaching; 2. the anaerobic conditions in the manure pack, with nitrogen in the ammonium form, and the generally high pH, promotes denitrification and inhibits biological nitrate formation. As noted by Hallberg and other (1983), runoff from active feedlots in the Big Spring basin contains less than 5 mg/l nitrate. When the manure pack is removed from the feedlot, or when the feedlot is no longer populated oxidizing conditions will develop and pH may decrease promoting nitrate formation and leaching, but the effects of this are

Table 16. Measured nitrate concentrations and calculated nitrate-N stored in soils under various landuse in the Big Spring basin; summarized by depth.

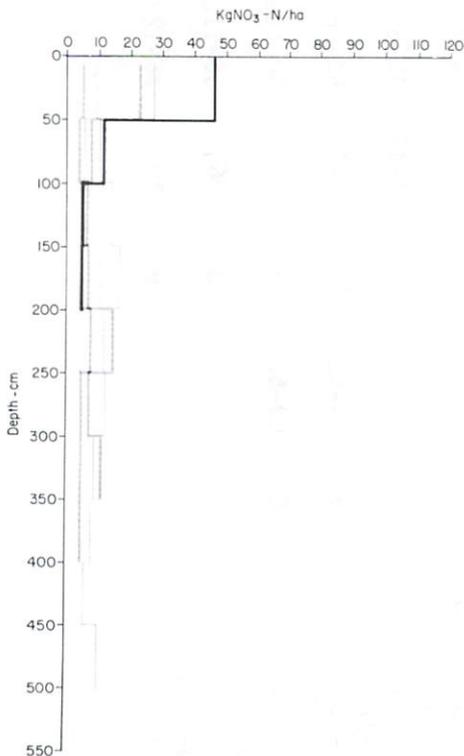
Depth cm (inches)	Landuse														
	Forest-Wood lot			Pasture/Fertilized Pasture/Alfalfa Alfalfa-Grass Haycrop			Low-Fert. Corn in Rotation			Hi Fertilization Corn					
	NO ₃ mg/kg	NO ₃ -N kg-N/ha	Cumula- tive kg-N/ha	NO ₃ mg/kg	NO ₃ -N kg-N/ha	Cumula- tive kg-N/ha	NO ₃ mg/kg	NO ₃ -N kg-N/ha	Cumula- tive kg-N/ha	1982*			1983		
									NO ₃ mg/kg	NO ₃ -N kg-N/ha	Cumula- tive kg-N/ha	NO ₃ mg/kg	NO ₃ -N kg-N/ha	Cumula- tive kg-N/ha	
0-20 (0-8)	34-36	19-20	19-20	7-19	4-12	4-12	4-33	3-20	3-20	31-74	19-45	19-45	5-14	3-9	3-9
20-50 (8-20)	4-9	3-7	22-27	6-16	5-11	9-23	2-24	2-22	5-42	17-55	27-55	46-100	4-32	6-23	9-32
50-100 (20-40)	3-5	5-7	27-34	5-12	10-12	19-35	2-22	4-36	9-78	17-70	28-90	74-190	8-28	18-46	27-59
100-150 (40-60)	2-4	4-5	31-39	6-11	11-14	30-49	3-13	7-20	16-98	43-70	22-115	96-305	18-19	30-31	57-116
150-200 (60-80)	3-4	6	37-45	6-10	10-16	40-65	8-9	12-14	28-112	10-36	16-59	112-364	7-19	13-23	80-139
200-250 (80-100)	4	7	44-52	3-7	4-12	44-77	4-9	7-14	35-126	9-32	15-54	127-418	9-36	15-63	95-202
250-300 (100-120)	3	5	49-57	3-7	4-12	48-89	4-9	7-14	42-140	0.3-18	1-32	128-450	22-27	36-48	131-250
300-350 (120-140)	3	5	54-62	3-5	4-9	52-98				7-12	12-21	140-471	15-22	30-36	161-286
350-400 (140-160)	3	5	59-67	5	8	60-106				7	12	152-483	15-17	28-30	189-316
400-450 (160-180)				3	6	66-112							14	24	213-340
450-500 (180-200)				6	10	76-122							22	39	252-379
500-550 (200-220)													8	14	266-393

*The low range values come from a field in the 2nd year of corn after a meadow rotation. Other data from areas of 4 or more years of corn and chemical N-application, at a rate of approximately 165-200 kg-N/ha (150-175 lbs-N/acre).



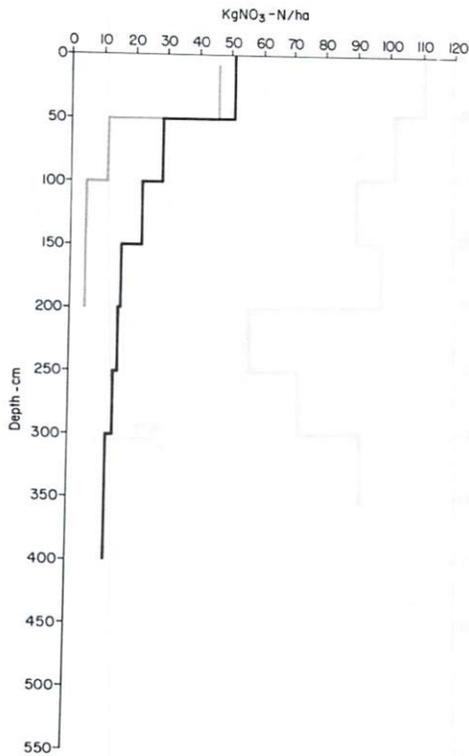
A. (Above) Forested areas.

B. (Above) Bold black line, 2nd year alfalfa hay in low-fertilization corn rotation; light solid line, pasture with scattered timber; dashed lines fertilized pasture; gray lines from A. for comparison.

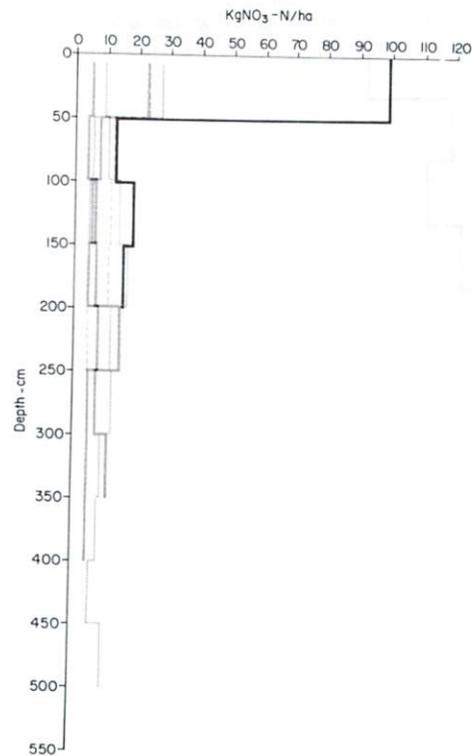


C. (Left) Bold black line shows profile under first-year, high-fertilization corn, after clearing of forest; gray lines from A and B for comparison.

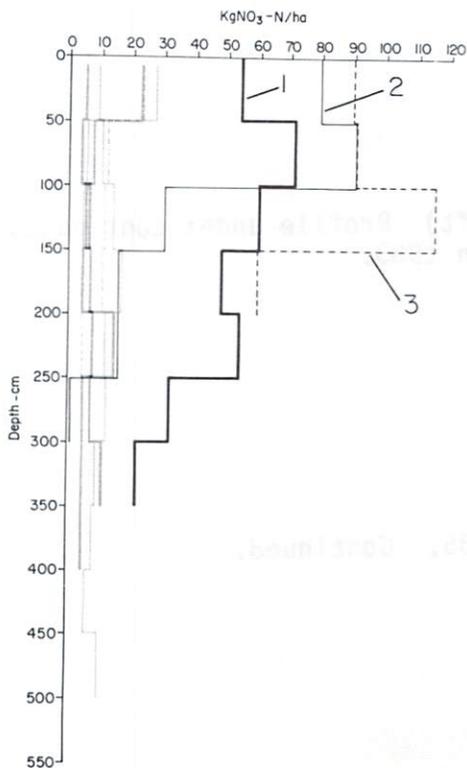
Figure 35. Depth distribution of nitrate stored in soil profile under different landuse; summarized as Kg-NO₃-N/ha in 50 cm increments.



D. (Above) Bold black line shows 2nd-year corn after alfalfa-meadow rotation; gray lines from 35A for comparison.

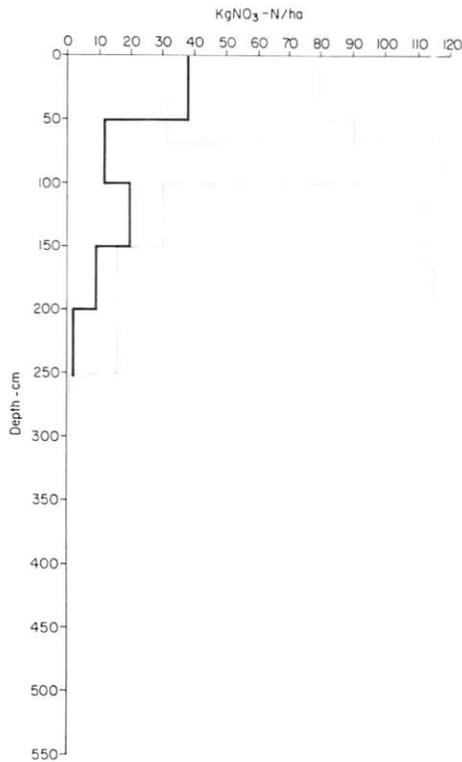


E. (Above) Bold black line shows profile under a feedlot; gray lines from 35A and B for comparison.

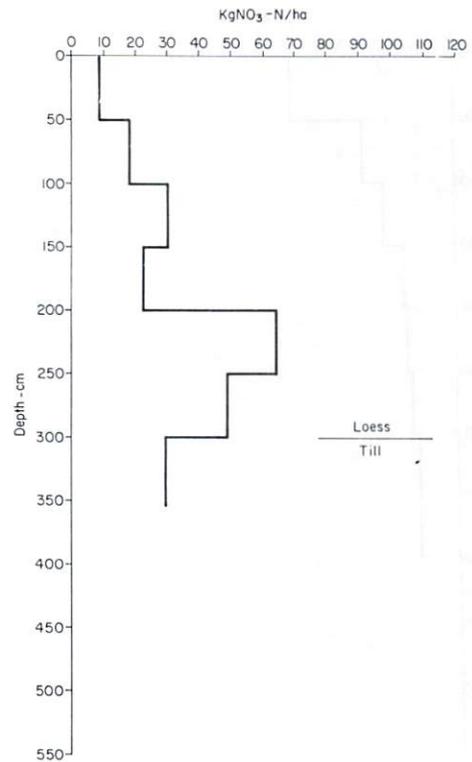


F. (Left) Black lines (1. bold, 2. light, 3. dash) show profile under high-fertilization continuous corn, sampled in 1982; gray lines from forest and pasture (35A and B) for comparison.

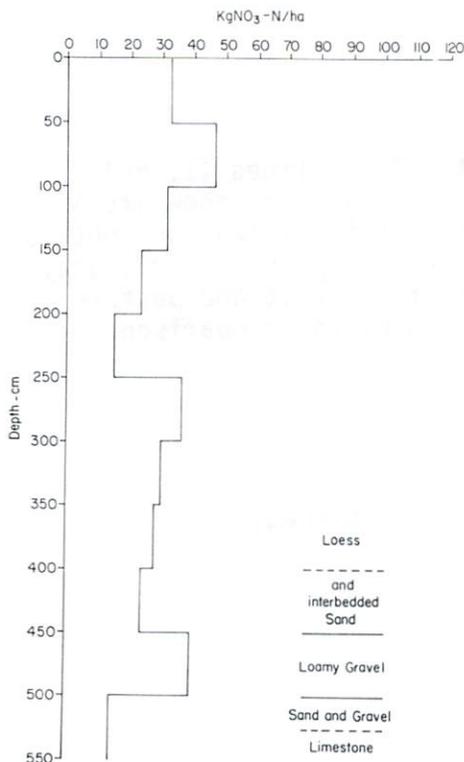
Figure 35. Continued.



G. (Above) Comparison of 1982 and 83 data from continuous corn, same location; data are average of duplicate cores; bold line 1983, light line 1982.

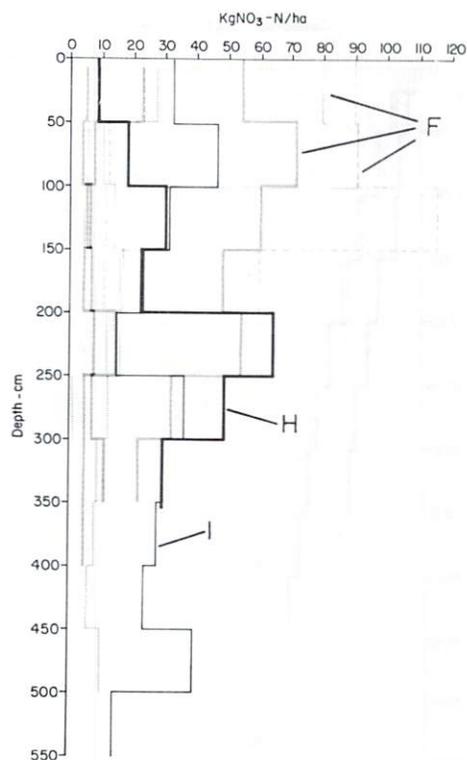


H. NO₃-N profile under continuous corn, 1983.



I. (Left) Profile under continuous corn 1983.

Figure 35. Continued.



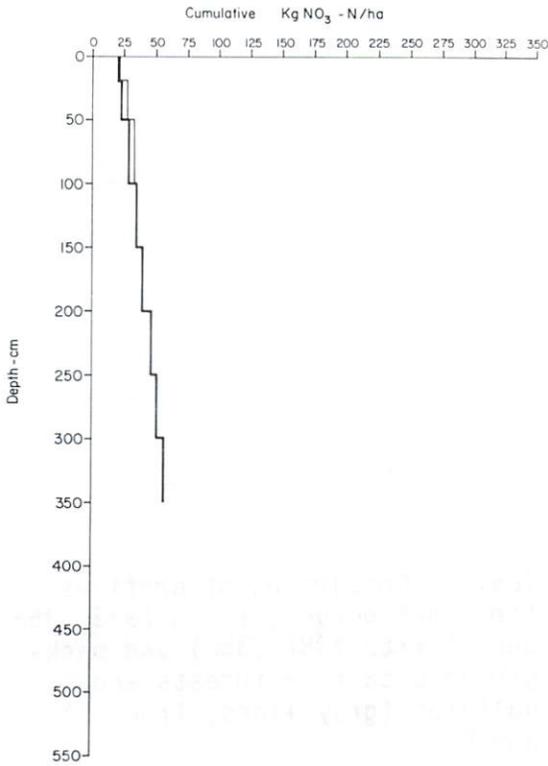
J. (Left) Comparison of profiles from continuous corn in 1983 (35H and I) with 1982 (35F) and background data from forests and pastures (gray lines, from 35A and B).

Figure 35. Continued.

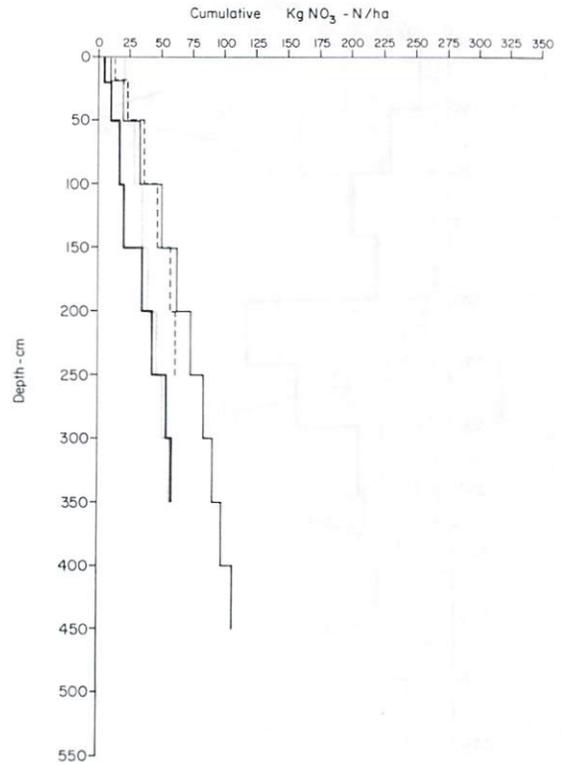
generally localized (Mielke and Ellis, 1976).

Figures 35F and 36F show the $\text{NO}_3\text{-N}$ concentration and accumulations from three representative sites of continuous corn (see Table 16). These soils show much higher concentrations and accumulations of $\text{NO}_3\text{-N}$ than the background data or the rotation corn sites, to depths of 3.5 m (site 1), but particularly in the upper 1 to 2 m. Site 3 (figures 35F and 36F) terminated in gravel overlying the Galena aquifer and thus large quantities of $\text{NO}_3\text{-N}$ (350 kg/ha at 2.0 m) are available to be leached directly into the aquifer. Site 2 shows another variation. Site 2 is located in alluvial soils along Roberts Creek, near sampling site 110 (F-45; see figure 3) and the water table was encountered at about 2.5 m (8.2 ft.). Nitrate-N concentrations are quite high near the surface but decline just above the water table, and at the water table drop to very low values.

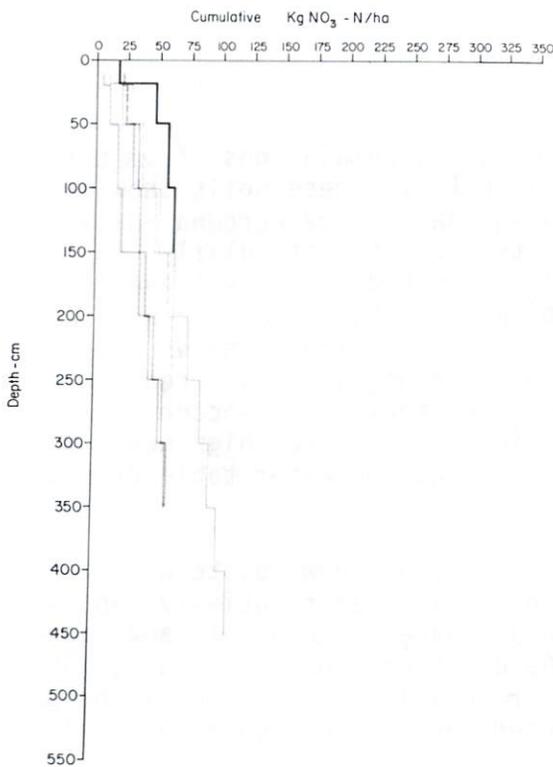
The continuous-corn sites sampled after harvest in 1983 show quite different $\text{NO}_3\text{-N}$ distributions. During 1982 the growing season had relatively normal precipitation and few rainfall-infiltration-discharge events of any consequence occurred (Hallberg et al., 1983). As described in this report, 1983 had greater rainfall and a number of large rainfall-infiltration-discharge events occurred up through early July. As noted these events moved a considerable mass of $\text{NO}_3\text{-N}$.



A. (Above) Forested areas.

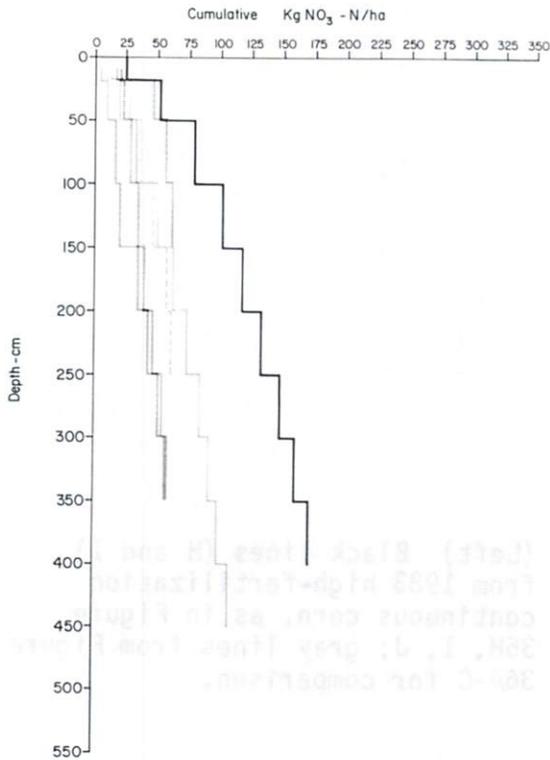


B. (Above) Black lines are alfalfa hay, pasture with timber, fertilized pasture, as in Figure 35B; gray lines from 36A for comparison.

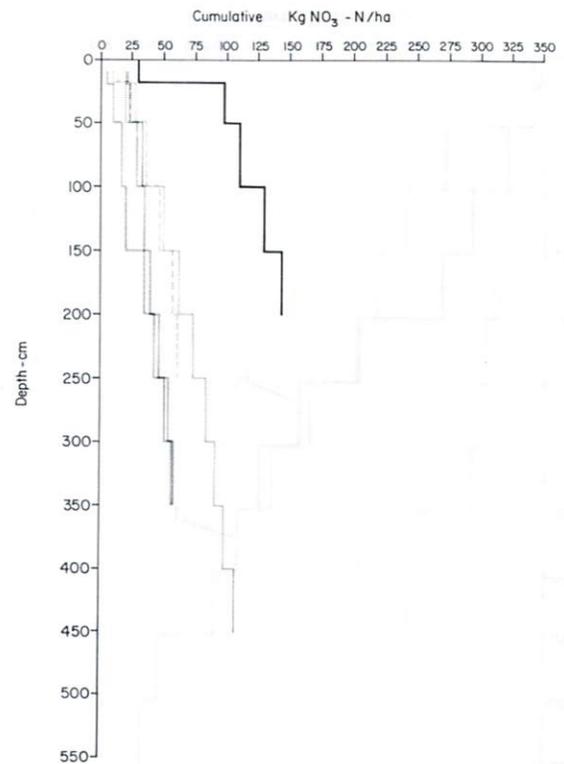


C. (Left) Bold black line, first-year high-fertilization corn after forest clearing, as in Figure 35C; gray lines from 36A and B, for comparison.

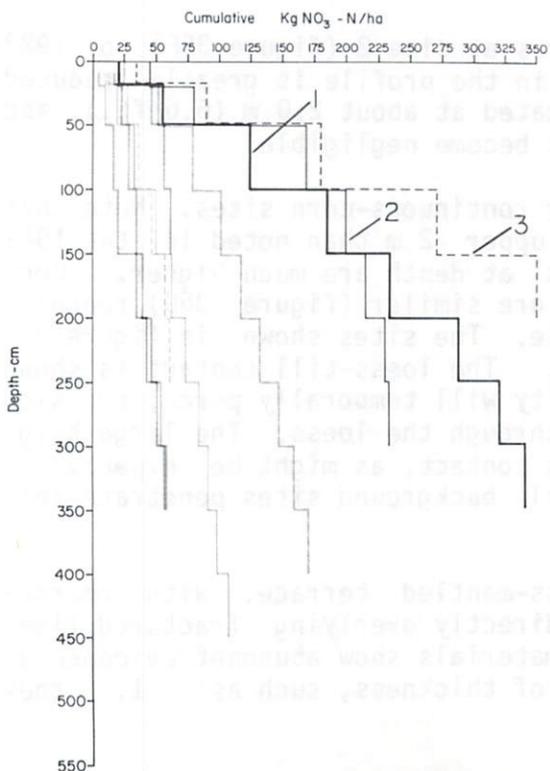
Figure 36. Cumulative kg-NO₃-N/ha stored in soil profile under different landuse; compare with figure 35.



D. (Above) Black line - second year corn after alfalfa rotation, as in Figure 35B; gray lines from 36A-C for comparison.

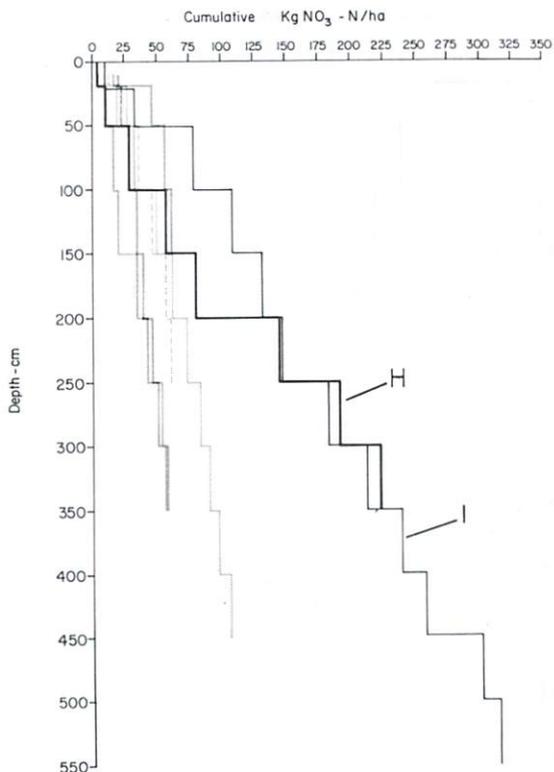


E. (Above) Black line - from feed lot as in Figure 35E; gray lines from Figure 36A and B for comparison.



F. (Left) Black lines (1-3) from 1982 high-fertilization, continuous corn, as in Figure 35F; gray lines from Figure 36A-D for comparison.

Figure 36. Continued.



G. (Left) Black lines (H and I) from 1983 high-fertilization continuous corn, as in Figure 35H, I, J; gray lines from Figure 36A-C for comparison.

Figure 36. Continued.

Figure 35G shows the data from replicate cores at site 2 (figure 35F) for 1983 and 1982. In 1983 the mass of $\text{NO}_3\text{-N}$ found in the profile is greatly reduced from 1982. In 1983 the water-table was located at about 2.0 m (6.6 ft.), and at that point again $\text{NO}_3\text{-N}$ values in the soil become negligible.

Figure 35H and 35I (and 35 J) show two other continuous-corn sites. Note that $\text{NO}_3\text{-N}$ concentrations are much lower in the upper 2 m than noted in the 1982 samples. However, the $\text{NO}_3\text{-N}$ concentrations at depth are much higher. Consequently, the cumulative affects at depth are similar (figure 36G) reaching levels of 200 to 350 kg-N/ha in the profile. The sites shown in figure 35H and I show some other interesting patterns. The loess-till contact is shown on figure 35H. This lithologic discontinuity will temporally perch, or slow the vertical movement of water percolating through the loess. The large bulge in $\text{NO}_3\text{-N}$ accumulation occurs just above this contact, as might be expected in a year of deep infiltration. (Note several background sites penetrate this contact but do not show such a feature.)

The site shown in figure 35I is on a loess-mantled terrace, with coarse-textured (and permeable) sand and gravels directly overlying fractured limestone of the Galena aquifer. The loess materials show abundant evidence of water movement throughout their 4 m (13 ft) of thickness, such as: 1. they

are leached of carbonate minerals; 2. obvious vertical partings (joints or prism boundaries) or macropores were encountered to depth; and 3. silt and clay coatings were present on these partings providing evidence for translocation along them. Also, as will be described in the next section, residues of atrazine, 0.3 ug/kg, were detected below 4 m (13 ft) in depth. Note that relatively high $\text{NO}_3\text{-N}$ concentrations occur all through this profile, down to the contact with the limestone aquifer at about 5.5 m (18 feet). At this site leaching of nitrate and herbicides is obviously taking place, and delivering these surficially derived chemicals into the aquifer through a substantial thickness of material.

These deep cores provide proxy evidence of what is happening in areas where the soils and glacial deposits are much thinner over the aquifer. If the fractured and karstified limestone of the Galena aquifer were in place at 2m (6.6 feet) under each of these sites the large nitrate accumulations noted in the soils, would have leached directly into the aquifer. Table 17 shows data from three analogous sites where the aquifer occurs within the soil profile, at depths of 0.6 to 1.1 m (1.8 -3.4 ft). These sites show the same trends in $\text{NO}_3\text{-N}$ as do their thicker counterparts (Table 16, figures 35 and 36), but the profiles end in rock.

Returning to the data in Table 16 the cumulative ranges of $\text{NO}_3\text{-N}$ from all the core sites is summarized by landuse. At a depth of 1.5 m (5 feet) the $\text{NO}_3\text{-N}$ stored in the soil under forest ranges from about 30-40 kg-N/ha (25-35 lbs-N/ac), 30-50 kg-N/ha (25-45 lbs-N/ac) under pasture-alfalfa-meadows, and from 16-100 kg-N/ha (14-90 lbs-N/ac) under low-fertilization, rotation corn. There is almost no overlap with the high-fertilization corn sites in 1982 which ranged from about 95-300 kg-N/ha (85-270 lbs-N/ac); even in 1983 these sites were higher ranging from about 60 to 110 kg-N/ha (55-98 lbs-N/ac). At 3 m (10 feet) depth the forest-pasture-alfalfa-meadow areas range from about 50 to 90 kg-N/ha (45-80 lbs-N/ac), the low-fertilization corn from 40 to 140 (35-125 lbs-N/ac), while the continuous corn from both 1982 and 1983 range from 130 to 450 kg-N/ha (115-400 lbs-N/ac).

These results are in full agreement with numerous agronomic studies of the $\text{NO}_3\text{-N}$ buildup in soils, directly related to longevity and rate of fertilization. Some of these studies will be reviewed in a subsequent section.

Soil Pesticides

The soil profiles were not analyzed for pesticide residues in the same detail as for nitrate. The data from the soil-pesticide analyses are summarized on Table 18, by depth in the soil profile. Atrazine, Bladex, Lasso, the herbicides almost ubiquitously used in the area were all detected in surface soil samples (0-8 inches, 20 cm), as were Dyfonate (the second or third most commonly used insecticide in the basin) and dieldrin. Only atrazine was found below a depth of 50 cm (20 inches) in any of the cores. Atrazine residues as high as 1.0 ug/kg were detected to depths of 3.0 m (10 feet) and as noted 0.3 ug/kg atrazine was detected from one site at a depth of 4.4 m (14.5 feet). These concentrations are similar to the persistent concentrations of atrazine

Table 17. Nitrate-N stored in "shallow loess" derived soils over bedrock. Concentrations in kg NO₃-N/ha for depth interval of soil.

Depth cm (inches)	Forest	Low-Level N-Fertilization; 2nd year corn in rotation	Fertilized Continuous Corn
0-20 (0-8)	20	15	21
20-50 (8-20)	7	12	20
50-100 (20-40)	5	(rock)	47
	(rock)		(rock)

now found in the groundwater year-round in the basin. In the Floyd-Mitchell county area Lasso and Sencor have been detected at depths up to 66 cm (26 inches) under soybean fields in very limited sampling, by Libra and others (1984).

NITRATE AND PESTICIDE ANALYSES FROM IGS PIEZOMETERS

In the fall of 1982 the authors installed 15 piezometer tubes; 10 in the upland loess and 5 in alluvial soils and deposits along Robert's Creek. The depths of the open interval in the wells ranged from 1 to 2 feet (0.3-0.6 m) in depth to 15 to 16 feet (4.6-4.9). No perched water table was encountered in the upland loess in the dissected terrain which marks the basin. The wells were designed with an inner collection tube below the slotted-screened intervals in hopes that as "slugs" of water (during intermittent saturated conditions with infiltration recharge events) passed through the soil profile enough water might enter the well to be analyzed for water-quality. Unfortunately, not enough water collected in the upland sites for analysis.

The alluvial well sites provide some interesting data which are worthy of discussion. One well was installed near surfacewater sampling site 111 (F-47; see figure 3) along Robert's Creek. This is in a 'losing' reach of Robert's Creek, where the potentiometric surface in the Galena aquifer is considerably below Robert's Creek. The well was installed in the alluvium, finished in sand and gravel approximately 5 feet (1.8 m) below the bed of Robert's Creek. The bore-hole and the well in the alluvium were (and are

still) dry, even though Robert's Creek flows perennially past this site less than 50 feet (15 m) away. As noted by Hallberg and others (1983) the bed of Robert's Creek is likely sealed with fine-grained material (silt and clay) such that it does not lose its entire flow through this reach. The base-flow of the creek is maintained by shallow groundwater flow and tile-drainage in the upper portion of the basin. The soils at this site were analyzed for nitrate and the results are shown as site 3 on figures 35F and 36F. As noted in the prior discussion high concentrations of nitrate occur down to the alluvial gravels which directly overlie the Galena aquifer, and thus large quantities of nitrate (350 kg/ha at 2.0 m) can obviously be leached rather directly into the aquifer.

Denitrification In An Alluvial Aquifer

Another series of piezometers were installed near surfacewater sampling site 110 (F-45; figure 3) along the upper, gaining reaches of Robert's Creek. Three wells have been installed: well 8, with a screened interval at 8.7-9.7 feet (2.7-3.0 m) below the landsurface, and when installed (11/4/82) the water table was about 2.5 feet (0.8 m) below the surface; well 9, lateral to well 8, in a lower elevation swale on the alluvial surface, the well is open at a depth of 1.1 to 1.8 ft. (0.3 -0.5 m) in an interval of peat to peaty silt; well 8A was installed in 1983 to the same total depth as well 8, but it is slotted and screened throughout its depth. The water-quality analyses for these sites are given on Table 19 along with data from the same date from Robert's Creek (F-45) which flows past these sites. The soil-nitrate data from site 8 (and 8A) is shown as site 2 in figures 35F, 35G, and 36F. As noted for both 1982 and 1983 there was significant amounts of available nitrate in the soil profile, but this declined to negligible values at the water table. This site has been in continuous corn under a high rate of fertilization for at least 5 years.

The water samples from well 9 have always shown <5 mg/l nitrate, and water samples from well 8 have shown <5 mg/l nitrate in over 70 percent of the samples, while the adjacent stream (which is recharged by the groundwater from this alluvial aquifer) has exhibited nitrate concentrations ranging from 32 to 68 mg/l. Only during periods of rainfall and high infiltration (May and July 1983) has well 8 shown any significant nitrate concentrations (6-40 mg/l). Well site 8A was installed to sample water from the top of the water table at this site, in case the nitrate was concentrated and moving laterally at the top of the groundwater in the alluvial aquifer. No nitrate (<0.5 mg/l NO₃ from detailed analyses) has been detected in this well either.

Other alluvial groundwater sites (from tile lines or other shallow wells) have exhibited nitrate concentrations ranging from about 40 to 150 mg/l at comparable times. Well sites LA-1 and LA-2 were installed in an alluvial aquifer near surfacewater and tile-drainage water sampling sites L-23S (109) and L-22T (108) to compare to wells 8 and 9. The data for these sites is also shown on Table 19. The analyses from these two sites, which sample the top one foot (0.3 m) of the water table, ranged from 72 to 148 mg/l NO₃ at the same time as wells 8, 8A, and 9 showed <5 mg/l. Note that the streams adja-

Table 18. Pesticide concentrations in loess soils under "continuous" corn; samples taken after harvest in fall of year. Concentrations in $\mu\text{g}/\text{kg}$ of soil.

Depth cm (inches)	1982	1983
0-20 (0-8)	3.6 - 120.0A ND - 5.8B ND - 23.0L ND - 10.0F ND - 15.0N	11.0 - 100.0A ND - 5.8B ND - 15.0L ND - 2.1F 0.6 - 2.0N
20-50 (8-20)	1.0 - 1.4A	6.0 - 18.0A 2.1L - 2.4L
50-100 (20-40)	1.0 - 12.0A ND - 1.8N	ND - 6.0A
100-200 (40-80)	ND - 1.1A ND - 0.8N	ND - 2.6A ND - 0.5N
200-300 (80-120)	ND - 1.0A	
400-500 (160-200)		0.3A

A - atrazine; B - Bladex; L - Lasso; F - Dyfonate; N - dieldrin;
ND - none detected.

cent to each site exhibit similar nitrate concentrations (38 and 43 mg/l).

The nitrate concentrations from LA-1 and LA-2 range from 13 to 73 mg/l higher than the tile-line (L-22T) which drains part of the same area of the alluvial soils. This would be expected because the tile-drainage would integrate water at greater depth, and water infiltrating below fence rows and field-end rows which are in meadow around this area.

There is little significant difference in the amount of $\text{NO}_2\text{-N}$ and ammonium-N in the groundwater from these sites; and highest $\text{NO}_2\text{-N}$ and ammonium-N occur at the sites with the highest $\text{NO}_3\text{-N}$. The organic-N is related to the amount of suspended-sediment that has seeped through the screening into the well (the wells are generally finished in the fine-grained, silty alluvium which mantles the sand and gravels of the alluvial deposits).

The pesticide analyses from these groundwater samples provide some insight into the phenomenon affecting the water-quality in these alluvial settings.

Table 19. Water-quality analyses from alluvial wells in the Big Spring basin. Data from adjacent surfacewater and tile lines shown for comparison. Analyses reported for nitrate as NO₃ in mg/l (unless noted otherwise), nitrate-N, organic-N, and ammonium-N, as N in mg/l. Pesticide data in parentheses, in µg/l, with letter abbreviation for pesticide species (A - Atrazine, etc.). (For wells 8, 9, 8A, LA-1, and LA-2 the well which was sampled for pesticides is also noted in the parentheses.)

Date	Wells			Stream	Stream	Tile	Wells	
	8	9	8A	F-45 (110)	L-23S (109)	L-22T (108)	LA-1	LA-2
<u>1982</u>								
11/30	<5	<5		40	42	72		
	(8 - 0.15 µg/l A-atrazine)							
12/29	<5	<5		38	51	79		
	(8 - 0.30A)							
	(9 - atrazine present, but organic interference would not allow quantification)							
<u>1983</u>								
5/4	6	<5		38	50	66		
	(8 - 0.20A)			(0.20A)	(0.24A)	(0.24A)		
5/19	40	<5		48	52	78		
	(8 - 2.1A, 0.3B-Bladex)							
	(9 - atrazine present, interference as noted above)							
6/28	<5	<5		45	48	72		
				(8.0A)				
				(0.49B)				
				(3.0L- Lasso)				
				(2.1D - Dual)				
6/29				62	54	91		
6/30				32	68	107		
7/6	12	<5			87	91		
	(8 - 1.0A, 0.11B)				(0.93A)	(1.20A)		
					(0.10B)	(0.11B)		
						(0.12L)		
11/2								
1300	<5	<5	<5	68				
1700	<5	<5	<5					
11/3	<5	<5	<5		50	76	148	94
	(8A - 0.15A)							
12/12	<5	<5	<5		44	63	136	85
12/13	(N-Series analyses)							
NO ₃	2.7	<0.5	<0.5	38	43	59	122	72
(NO ₃ -N)	(0.6)	(<0.1)	(<0.1)	(8.5)	(9.5)	(13)	(27)	(16)
NO ₂ -N	0.17	0.06	0.09	0.20	0.12	0.28	0.34	0.27
Org-N	7.2	11.0	0.82	0.23	<0.01	<0.01	28	7.1
Amm-N	0.06	0.05	<0.01	0.07	<0.01	<0.01	0.38	0.07
	(8A - 0.20A)						(LA-1 - 0.30A)	

Every water sample from wells 8, 8A, and 9 analyzed for pesticides showed concentrations of atrazine in the range typical (0.15 -2.1 $\mu\text{g/l}$) for shallow groundwater in the Big Spring basin. The analyses from these wells are nearly identical to those from alluvial wells LA-1 and -2, and from the tile-line (e.g., L-22T) and the adjacent surfacewater sites (particularly during base-flow). During infiltration recharge periods, when the groundwater in well 8 exhibited nitrates atrazine concentrations rose (to 1.0 -2.1 $\mu\text{g/l}$) and Bladex was detected also; again the concentrations are nearly identical to tile-effluent pesticide concentrations where nitrates are always present. The consistent presence of pesticides in the water in the alluvial aquifer clearly suggest that the nitrate present in the upper, aerobic portion of the soil column is denitrified at or near the water-table; this suggests an abrupt, active anaerobic interface near the water table in this setting (see Khdyer and Cho, 1983; Robbins and Carter, 1980). The nitrate must be denitrified and lost from the system as N or N_2O gas. Although ammonium-N may be stable with these conditions little N as ammonium (as would be expected) is being transported to this depth (Table 19).

Why is denitrification occurring in the area of wells 8 and 9 and not in other areas such as LA-1 and -2, or other areas that have been investigated? The area around wells 8 and 9 is not tile-drained. It is possible that tile drainage in some of the other alluvial areas, as it lowers the water table and accelerates the movement of water through the soil, enhances aerobic conditions and shortens the residence time, thus limiting or inhibiting denitrification (e.g., Baker and Johnson, 1977). However, the water table is at similar depths in some tile-drained areas as around wells 8 and 9, and during base-flow conditions is often relatively stable. We feel that differences inherent in the alluvial deposits may be a key factor.

Denitrification is a biogenic reaction requiring the proper microbial population and an adequate supply of oxidizable organic carbon. An adequate source of carbon may limit denitrification (e.g., Gambrell et al., 1975a and b). The alluvial deposits at the LA sites and the well 8 sites are similar in that they both have a mantle of 10 to 12 feet (3-3.6 m) of silt loam to light silty clay loam alluvium over sand and sand and gravel. They are very different in that the LA sites are in middle-Holocene age (ca. 4,000 -7,000 radiocarbon years before present) alluvium; these alluvial deposits exhibit strong oxidation (i.e., bright reddish-brown soil colors, abundant iron-oxide staining and mottling) and very little organic carbon except in the surface soil horizons, and in the base of the deposits. In contrast, the well 8 and 9 sites are located in late-Holocene (less than 3,000 RCYBP) alluvium. These deposits are marked by abundant organic carbon and organic debris interbedded within the alluvium; as noted well 9 was actually finished in a peat, silty-peat lens within the alluvium. With all this organic debris the mineral-sediments of the late-Holocene deposits all retain gleyed colors (reduced, greenish and gray colors). It seems most likely that the abundant organic carbon, and the anaerobic conditions it will help to produce, is the primary reason for the denitrification that must be taking place. During periods when large amounts of water and nitrate infiltrate to the water table the systems capacity to 'denitrify' is exceeded and nitrate does move into and through the alluvial-groundwater system, as shown by the analyses from well 8 (Table 19).

As discussed, and as shown on Table 19, the nitrate concentrations in the small streams in the Big Spring basin are generally 20% to 70% less than the

nitrate concentrations in tile-drainage water, and seepage water from fertilized-corn areas. Part of this reduction is related to the low nitrate inputs from pasture and meadow areas along the streams (e.g., nitrate concentrations from BTL-2D, figure 34), but some portion is also related to denitrification in the alluvial aquifer (such as in the area of wells 8 and 9) and possibly in-stream denitrification or N-use (e.g., Duff et al., 1984; Smith and De Laune, 1983; Swank and Caskey, 1982).

These observations point out two other important conclusions. First, the denitrification is another form of N-loss from the basin, and thus, as discussed, the mass of nitrate-N discharged in water from the basin is a minimum figure for the N-loss. Second, there is often an assumption that nitrate in well water or groundwater is an indication of the likelihood that pesticides may also occur. In these alluvial settings, where denitrification occurs, there are no nitrates, but pesticides do persist in the groundwater.

LANDUSE AND WATER-QUALITY CHANGES OVER TIME IN THE BIG SPRING BASIN

Changes in landuse, numbers of livestock, amounts of chemical fertilizer used, and groundwater quality in the Big Spring region have been reviewed by Hallberg and others (1983, 1984). Since these reports were issued some additional data have been compiled.

ASCS aerial photography of the Big Spring basin from 1970 was photo-interpreted to compile a landuse map and statistics to compare with similar data compiled for 1980 and reported by Hallberg and others (1983). The results are given in simplified categories on Table 20. In 1980, 22% more land area in the Big Spring basin--22.5 square miles or 14,4000 acres (5,800 ha)--was in corn (row crop, there are essentially no soybeans grown) than in 1970. Hallberg and others (1983) noted approximately a 40% increase in corn acreage over this time span from Clayton County statistical data, but also noted that according to most local experts the 40% figure was likely conservative. This is because the Big Spring Basin has a very high proportion of the 'prime' farm land in Clayton County, and the conversion from haycrops and pasture (and other cover crops) to more continuous corn was greater in this area than in the county in general. Though some of the differences between the 1970 and 1980 data may be related to rotation effects this is not likely to be substantial. Thus, the corn-acreage figures used to estimate the amount of fertilizer-N applied in the basin over time are also (as noted by Hallberg et al., 1983) conservative.

The other significant change detected was in the expansion of the area in strip-cropping. Although this valuable conservation practice is still only used on about 9% of the area, it increased 95% from 1970 to 1980; an areal increase of nearly 3,000 acres (1,200 ha).

In addition to the estimates of the amount of chemical and manure-N applied in the Big Spring basin over time, an "uncorrected" estimate of the maximum amount of N-harvested with the corn has been made. The results are shown on figure 37. These values were generated using the same statistics as used by

Hallberg and others (1983), with the following calculation (from A.M. Blackmer, Iowa State University, Agronomy Department, personal communication):

$$P_{fn} = (Y_f P_f - Y_u P_u) \times 0.56 / R$$

where,

- P_{fn} = percentage fertilizer N recovery in crop,
- Y = yields in bu/ac,
- P = percentage N in corn grain harvested, estimated as $P = 1.0 + (Y \times 0.004)$
- R = the rate of fertilization in lbs/ac

and the subscripts

- f = corn from fertilized plots
- u = corn from unfertilized check-plots

This calculation (derived by Blackmer from numerous test plot data) corrects the recovery values by subtracting the N removed in corn grown without fertilizer. These check data are not available for the Big Spring basin and thus the $Y_u P_u$ terms were dropped from calculations, providing an "uncorrected" or maximum estimate of the amount of N removed. These estimates simply amplify the prior relationships noted; from the late 1960's to the present the distance between the amount of N-removed by crops and the amount of fertilizer-N applied increases as the nitrate concentrations rise in the groundwater at Big Spring.

These relationships are not unique. The sharp increase in total chemical N-fertilizer use and rate of application seen in Iowa (figure 38a) is true for the entire corn-belt region. The average N-fertilization rate for corn across the cornbelt increased from about 65 lbs-N/ac (73 kg-N/ha) in 1965 to about 137 lbs-N/ac (153 kg-N/ha) in 1982 (Hargett and Berry, 1983). In Illinois similar trends have been noted. As shown in figure 38b since about 1965 more fertilizer-N has been added to cropland than was being removed in harvested crops. During this time the nitrate concentration in the Kaskaskia River increased concurrently with the increased fertilizer use (NRC, 1978). As reviewed by Libra and others (1984), such trends have been noted, beginning somewhat earlier, in Europe. Figure 38c shows the concurrent trends in the increased N-fertilizer use in France and the increase in nitrate concentration from a carbonate-groundwater spring in an agricultural area in France. These data show the same related, linear increases shown for Big Spring. The seemingly linear relationship between the increased application of chemical fertilizer-N and the nitrate in groundwater at Big Spring is consistent with a variety of standard agronomic research.

AGRONOMIC STUDIES OF N-FERTILIZATION AND LEACHING OF NITRATE BELOW THE ROOT ZONE

In past reports (Hallberg et al., 1983; Libra et al., 1984; Hallberg and

Table 20. Landuse change in the Big Spring Basin, 1970-1980. 1970 data from photo interpretation of 1970-ASCS aerial photography. 1980 from Hallberg et al., 1983. Figures shown in square miles and (%).

Landuse	1970		1980		% ¹ Change
	sq. miles	(%)	sq. miles	(%)	
Urban	3.37	(3)	3.45	(3)	
Forest	6.17	(6)	6.50	(6)	
Cover Crop	48.75	(47)	26.03	(25)	-22
terraced	2.32	(2)	2.13	(2)	
Strip Crop	3.27	(3)	7.55	(7)	+4
terraced	1.55	(2)	1.87	(2)	
Row Crop	30.97	(30)	49.15	(48)	+18
terraced	6.84	(7)	6.56	(6)	
	103.24	(100)	103.24	(100)	

¹ 1980%-1970% for significant differences.

Hoyer, 1982) the authors have reviewed a variety of research reports ranging from water-quality studies, to agricultural-engineering studies, to standard agronomic studies involved with crop yields, that show that losses of nitrogen, particularly as nitrate, below the root zone occur directly as a function of N-fertilization, particularly at high application rates. For example, in a review, Baker and Laflen (1983) note: "NO₃-N losses with subsurface drainage related in nearly linear fashion to N application for rates exceeding 50 kilograms per hectare." The intent here is not to verbally review the details of these studies again, but simply graphically display the results for comparison with the trends in groundwater-quality changes and fertilizer-rate increases noted in the Big Spring area.

This review will only use data from experiment-farm studies from the immediate Midwestern states: Iowa, Minnesota, and Wisconsin. These studies do not involve irrigated agriculture or any unusual soil conditions, which contribute to more rapid leaching of nitrate-N.

The results of the first group of studies are shown on figure 39. These studies all measured the relationship between the amount of fertilizer-N applied to the soil during continuous-corn cropping and the amount of NO₃-N that was stored in the soil profile to various (specified) depths over some

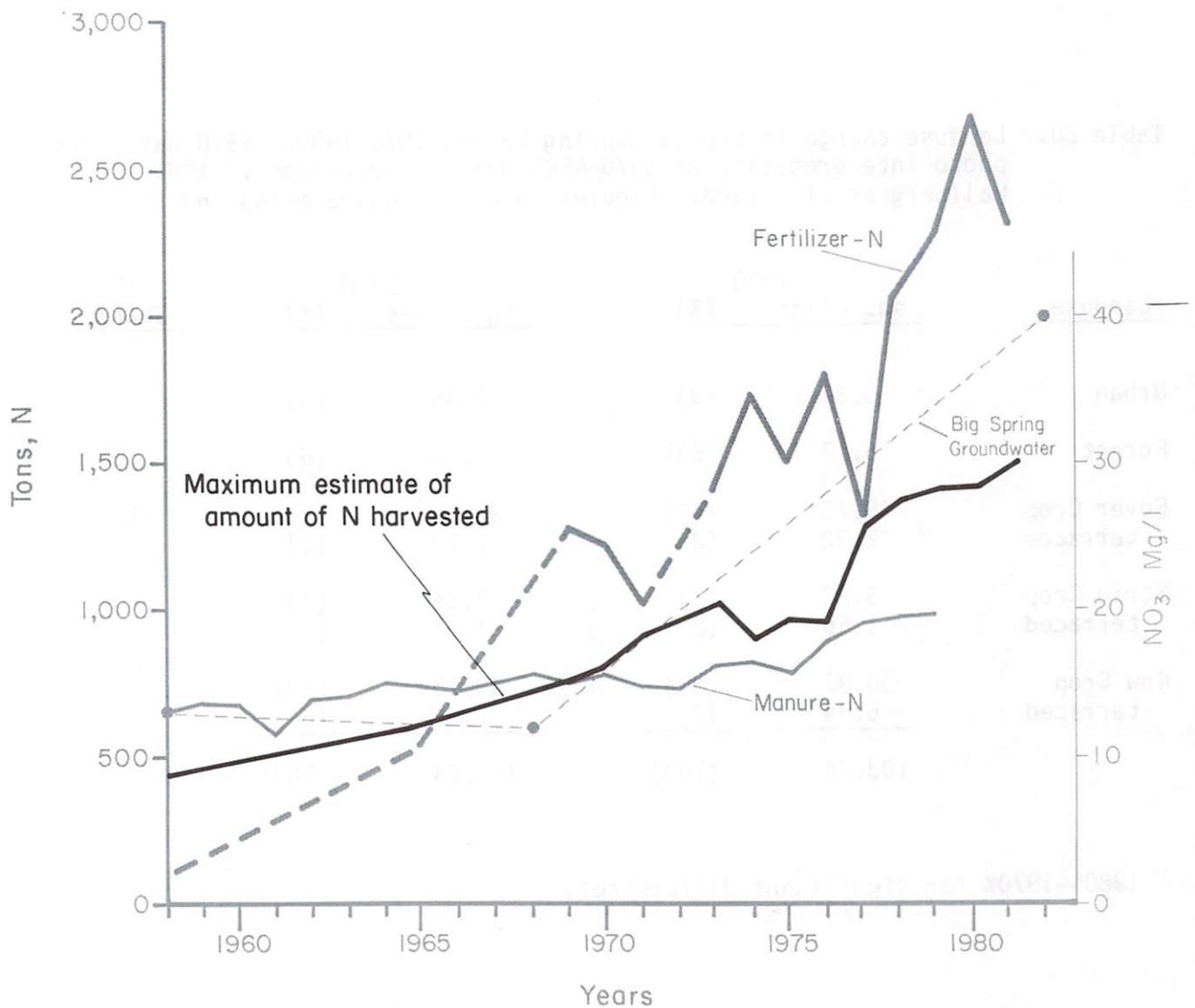
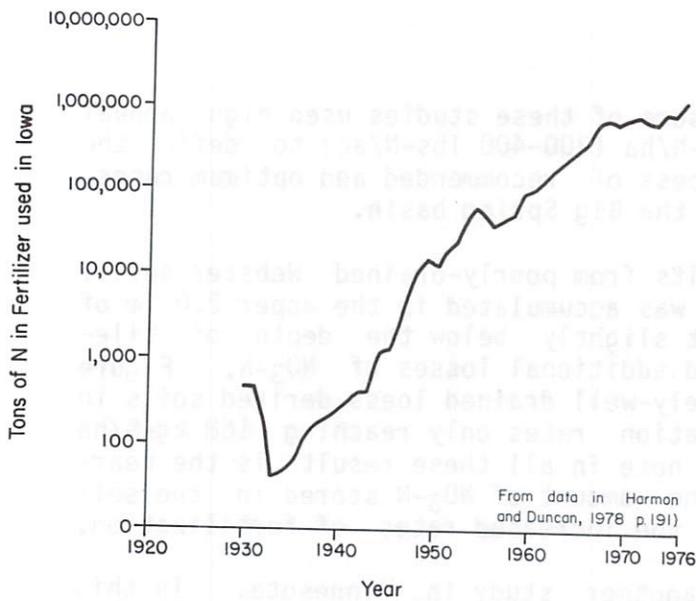
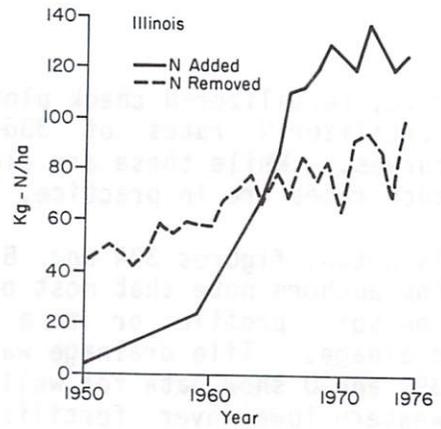


Figure 37. Estimated tons of fertilizer- and manure-nitrogen applied in the Big Spring basin, and average nitrate concentration in groundwater at Big Spring, shown in gray (from Hallberg et al., 1983, p. 160). Estimated maximum amount of N harvested with corn shown in black.

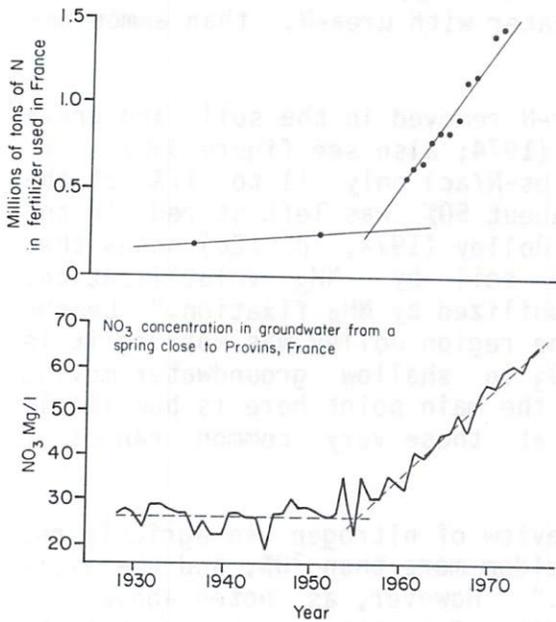
period of treatment. The horizontal (x) axis is the same on each diagram and shows the annual rate of fertilizer-N applied in kg-N/ha. The vertical (Y) axis shows the amount of NO₃-N (in kg-N/ha) that was measured in the soil profile, to the specified depth, at the end of the specified number of years of continuous treatment. The scale of the vertical axis varies from graph to graph because the soil depths and years of treatment vary among the studies. Figures 35A and B are good examples; both studies were conducted on poorly-drained Webster soils; the Minnesota study (figure 35A) measured the NO₃-N in the soil after 3 years to a depth of 3.0 m (10 feet), while the Iowa study measured the soil NO₃-N after 6 years but only to a depth of 1.8 m (5 feet). Note that most of these studies used an unfertilized, or very-low



A. Tons of nitrogen in fertilizer used in Iowa, 1929-1976.



B. Annual average addition of fertilizer N, and removal of crop N for corn in central Illinois (NRC, 1978).



C. Tons of N in fertilizer used in France, and nitrate concentration in a carbonate groundwater spring in an agricultural area (Pierre, 1983).

Figure 38. Increase in N-fertilizer use over time in Iowa, Illinois, and France in relation to N-removed in crops and groundwater quality.

rate, fertilizer-N check plot. Also, some of these studies used high annual fertilizer-N rates of 336 to 448 kg-N/ha (300-400 lbs-N/ac) to define the curves. While these are clearly in excess of recommended and optimum rates, such rates are in practice, locally, in the Big Spring basin.

As noted, figures 39A and B show results from poorly-drained Webster soils. The authors note that most of the $\text{NO}_3\text{-N}$ was accumulated in the upper 2.0 m of the soil profile; or to a depth just slightly below the depth of tile-drainage. Tile drainage water provided additional losses of $\text{NO}_3\text{-N}$. Figure 39C and D show data for well to moderately-well drained loess derived soils in western Iowa, over fertilizer-N application rates only reaching 168 kg-N/ha (150 lbs-N/ac). The important point to note in all these results is the nearly linear or curvilinear increase in the amount of $\text{NO}_3\text{-N}$ stored in the soil after corn harvest, in relationship to the increased rates of fertilization.

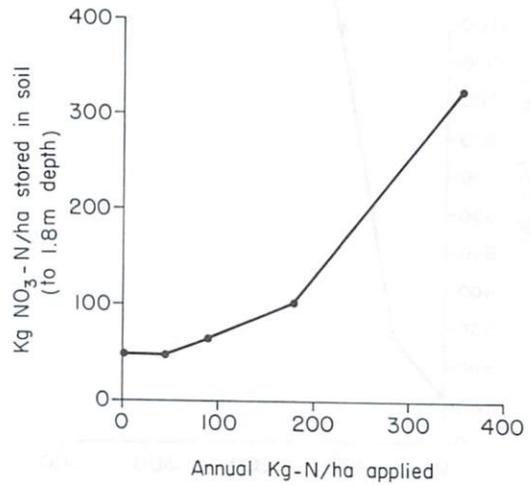
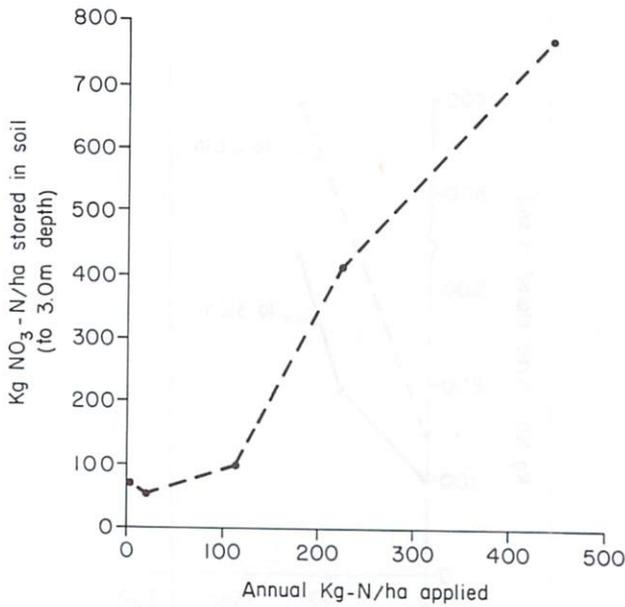
Figure 39E shows similar trends from another study in Minnesota. In this study (Nelson and MacGregor, 1973), the amount of N removed in the corn-grain was also measured. Note that the amount of N removed with the grain increases very little between application rates of about 100 and 200 kg-N/ha, while the amount of $\text{NO}_3\text{-N}$ accumulating in the soil continues to increase. Nelson and MacGregor also note: 1. that additional $\text{NO}_3\text{-N}$ was lost in tile-drainage water (an amount equivalent to about 35% of the fertilizer-N at the 196 kg-N/ha rate may be estimated from their data); 2. that little evidence indicated significant volatilization or gaseous losses of N; 3. greater N-losses, and slightly lower corn yields, were obtained with fall applied ammonium-nitrate; and that 4. corn N-uptake may be somewhat greater with urea-N, than ammonium-nitrate-N.

Figure 40 shows the percentage of fertilizer-N removed in the soil and grain for the 17-year Moody farm study by Jolley (1974; also see figure 39C). In the range of 112-168 kg-N/ha (100 to 150 lbs-N/ac) only 11 to 17% of the fertilizer-N was recovered in the grain; about 50% was left stored in the soil, and another 30% was not recovered. Jolley (1974, p. 126) notes that this 30% "was possibly lost from the soil by NH_3 volatilization, denitrification or surface runoff or was immobilized by NH_4 fixation." Leaching losses were not considered but even in the region Jolley was working it is likely that some of this N was lost as NO_3 in shallow groundwater moving laterally to discharge to streams. Perhaps the main point here is how little N was actually accounted for in the crop at these very common ranges of fertilization.

In this regard Keeney (1982, p. 632), in a review of nitrogen in agriculture, notes: "N recovery by agronomic crops is seldom more than 70%, and the average value is probably nearer to 50% . . ." However, as noted above for Jolley's study (1974), many published results for corn, suggest that N-recovery may more typically be in the range of 35% or less, particularly for continuous corn (e.g., Owens, 1960; Olsen et al., 1970; Jolley and Pierre, 1977; Chichester and Smith, 1978; Cooper et al., 1984).

The next group of studies (figure 41) reveals similar trends between the rate of N-fertilization and the amount of $\text{NO}_3\text{-N}$ lost in tile-drainage water, and the $\text{NO}_3\text{-N}$ concentration of the tile-drainage water.

Figure 41A shows results from a study in Minnesota and again the same linear



A. Minnesota; Webster CL; 3 years of treatment; Gast et al., 1978.

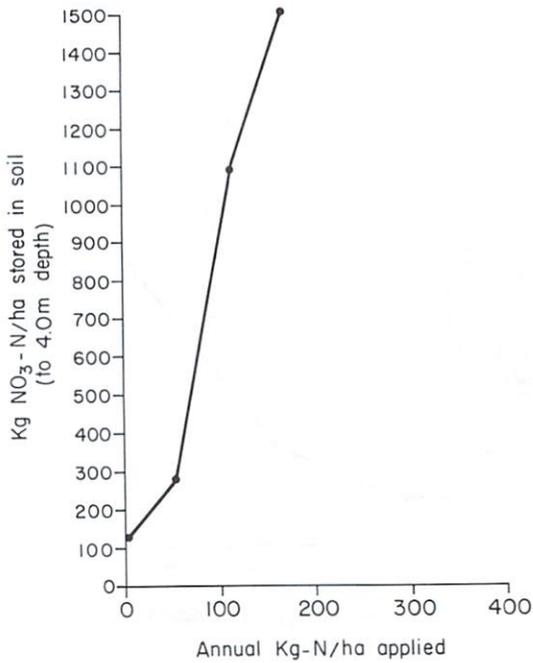
B. Iowa; Webster SiCL; 6 years of treatment; Jolley, 1976.

Figure 39. Midwestern experiment farm studies showing relationship between N-fertilization rate (kg-N/ha) and the amount of NO₃-N (kg-N/ha) stored in the soil to a given depth after specified time of treatment. The following are noted under each figure: the state; the soil type; the years of treatment; and the reference.

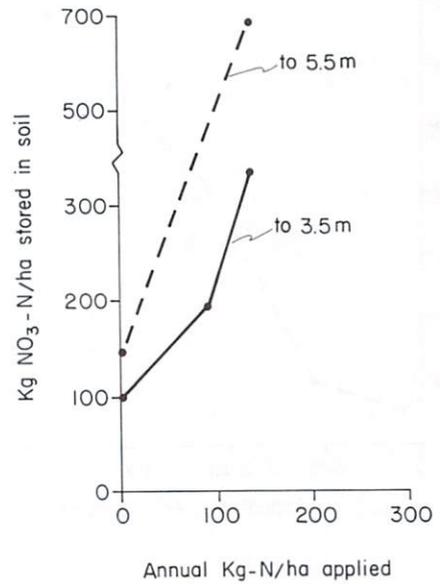
response between N-fertilization rate and N-leaching losses--reflected as NO₃-N lost through tile drainage--is apparent. Figure 41B and C show actual and model data from Iowa. Figures 41D and E show data from more recent companion studies in Minnesota; figure 41D shows the amount of NO₃-N lost in tile-effluent and the average concentrations; figure 41E shows the amount of NO₃-N stored in the soil after 5 years, and the percentage of fertilizer-N lost through leaching in tile-effluent as derived from nitrogen-isotope data. Again, the same linear trends are clear. Buzicky and others (1983) also note that the highest losses related to fall-applied N-fertilizer.

In relation to leaching losses related to tile-drainage Kanwar, Johnson, and Baker (1983, p. 1457) note:

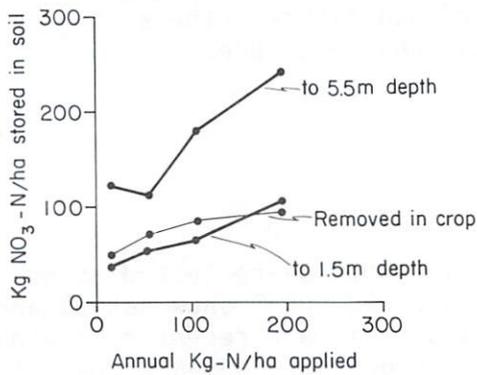
"Measured as well as predicted data indicate that an equivalent of nearly half of the applied fertilizer nitrogen is being discharged with tile drainage water. As farmers decide to apply more fertilizers to obtain higher yields, large leaching losses of nitrates can be expected to occur, an economic as well as an environmental concern."



C. Iowa; Moody SiCL; 17 years; Jolley, 1974.



D. Iowa; Galva and Sac SiCL; 14-16 years of treatment; Jolley, 1974.



E. (Left) Minnesota; Webster L; 10 years; Nelson and MacGregor, 1973.

Figure 39. Continued.

Leaching losses can also be affected by management differences. Figure 42 shows data from Burwell and others (1976) from studies in western Iowa. These studies compared effects of contour tillage and terracing; while terracing reduced surface runoff, sheet-rill erosion, and associated chemical losses in runoff, it substantially increased infiltration and subsurface water flow. As noted by the authors, and other studies, most NO₃-N losses occur in the in-

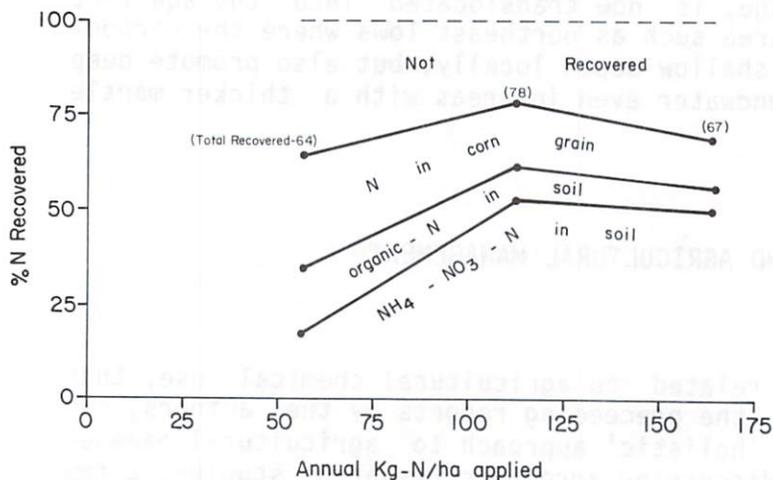


Figure 40. Percentage of fertilizer-N recovered in soil and grain (corrected for no-fertilizer-N check plot); Iowa; Moody SiCL; 17 years treatment; from Jolley, 1974.

filtration component, and hence the increased infiltration in these terraced areas greatly increased the losses of $\text{NO}_3\text{-N}$ (figure 42). As Burwell and others (1976) note, appropriate chemical management must be combined with conservation practices to minimize soil erosion and runoff as well as losses in "deep percolation" or groundwater. This statement is especially applicable for northeastern Iowa (as discussed by Hallberg and others, 1983) as well, where aquifers are particularly susceptible to contamination from the leaching of soil-applied chemicals.

In terms of management effects figure 43 shows the relationships among N-fertilization rate, $\text{NO}_3\text{-N}$ remaining in the soil, and rotation effects, for 4 end members in the rotation study of Olsen and others (1970). These authors found that the total amount of $\text{NO}_3\text{-N}$ in the soil profile, the distribution of $\text{NO}_3\text{-N}$ in the profile, and the amount of $\text{NO}_3\text{-N}$ below typical corn-rooting depth was directly related to the rate of N-application on corn, the number of years of corn in the rotation, and to some extent, the length of time since harvest of the last corn crop. They also note that a fallow year may promote excessive losses. Olsen and others (1970, p. 448) note that effective methods for limiting the amount of $\text{NO}_3\text{-N}$ leached to groundwater are: "limiting rates of N fertilizer to approximately that required by the crop, reducing the acreage and frequency of corn or other crops that receive fertilizer N in the rotation, and maintaining a crop cover on the land..."

Beyond these notes on management the important point of all these figures in relationship to the Big Spring data is that the linear response between the increased application of fertilizer-N and the increase in NO_3 concentrations in "shallow" groundwater (figure 37) is exactly what should be predicted from these standard agronomic studies. All of the studies reviewed (figure 38-43) were conducted in areas where aquifers are at substantial depth. If we insert an aquifer at depths of one to two meters into each of these studies, as is the case in extensive areas in northeastern Iowa, the $\text{NO}_3\text{-N}$ being 'stored' in

the soil, or lost in tile-drainage, is now translocated into the aquifer. This is particularly true for an area such as northeast Iowa where the carbonate aquifers are not only at very shallow depth locally, but also promote deep and rapid percolation of soil-groundwater even in areas with a thicker mantle of soil and Quaternary deposits.

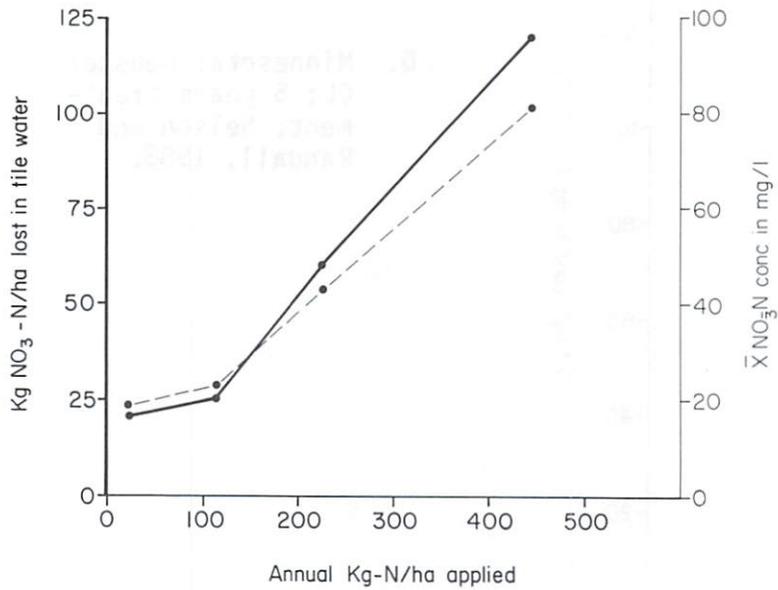
WATER QUALITY AND AGRICULTURAL MANAGEMENT

The groundwater quality problems related to agricultural chemical use, that are described in this report and the preceding reports by the authors, can only be resolved through a more 'holistic' approach to agricultural management. In the previous section, discussing agronomic research studies, a few comments of other authors were highlighted which pointed out that appropriate chemical management must be combined with soil conservation measures to adequately protect surfacewater quality, in particular. As discussed by Hallberg and others, (1983), we must also couple our standard concerns for soil conservation and surfacewater quality with the need to protect groundwater, as well. We must find ways to balance our need for efficient and profitable agricultural production with our need for safe drinking water.

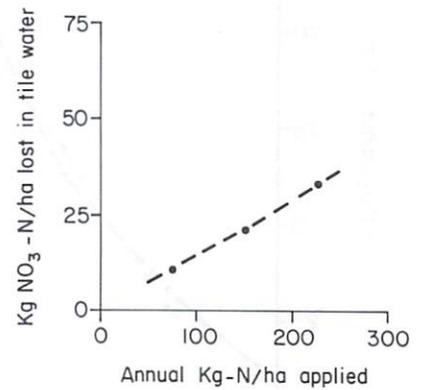
There are legitimate concerns for public health, over the long-term, if these water-quality problems continue or increase (see Hallberg and others 1983, p. 161-163 also). Pesticide concentrations are far below the toxic levels and generally well below levels thought to contribute to chronic problems. However, there are many uncertainties involved with the combinations of pesticides, and possibly their metabolites, which are occurring in groundwater, in relation to other environmental factors. Concerns for nitrate have generally been centered around drinking water for infants and the problems of methemoglobinemia. However, recent research suggests that high-nitrate drinking water may contribute to other long-term health problems in children and adults (e.g., Fraser and Chilvers, 1981). One recent epidemiological study suggests that nitrate concentrations below current standards may contribute to congenital (fetal) malformations (Dorsch et al., 1984). These studies are not definitive, but point out that there are many unknowns which need further research.

Beyond the health concerns and environmental impacts the magnitude of the chemical losses, particularly nitrogen, are of economic concerns as well. When crops (corn) are not utilizing 50% to 70% of the nitrogen applied there is obvious room for improved efficiency and economic gain. In this regard, the concerns reach much further than northeastern Iowa; the processes and losses documented in this report, for example, go on everywhere. Studies cited in the previous section were conducted in north-central Iowa and south-central Minnesota where the leaching of chemicals probably has not directly affected groundwater-drinking water supplies, but the same chemical inefficiencies are apparent.

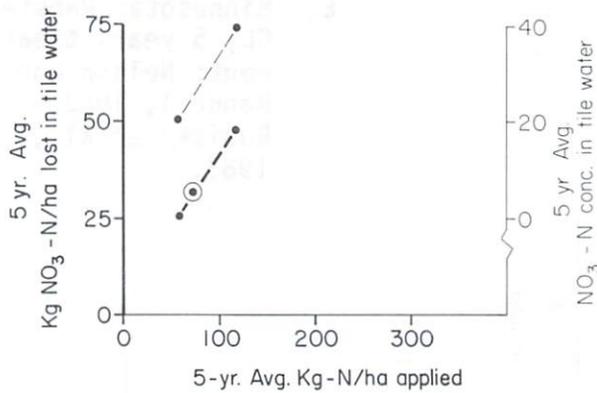
On the regional basis management alternatives should address not only soil conservation, but also the need to reduce chemical losses in infiltration. In the karst-carbonate aquifer region there are difficulties and trade-offs with



A. Minnesota; Webster CL; 3 years treatment; Gast et al., 1978.

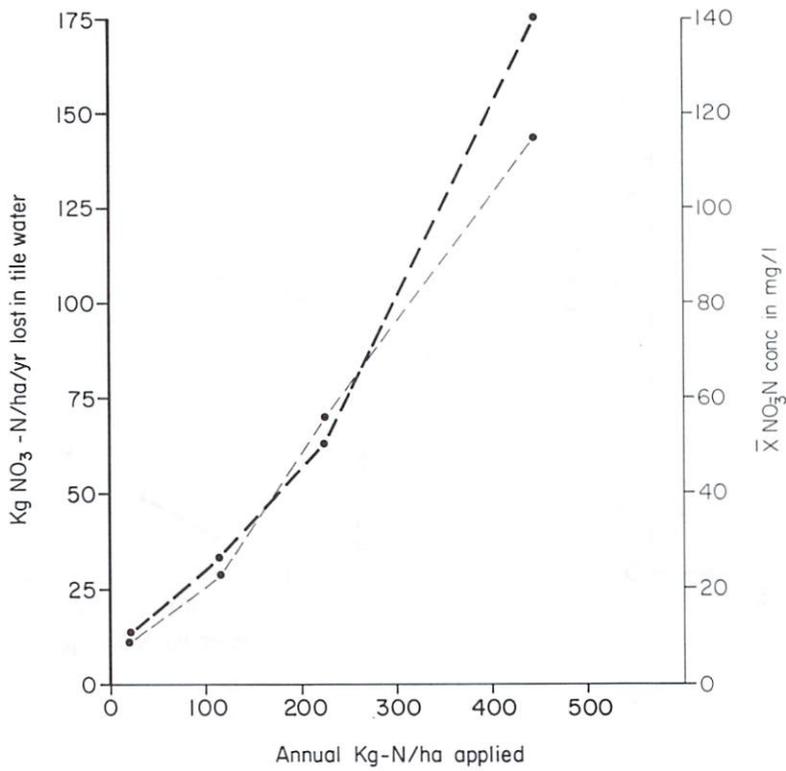


B. Iowa; Humboldt County-model data; Baker and Austin, 1982.

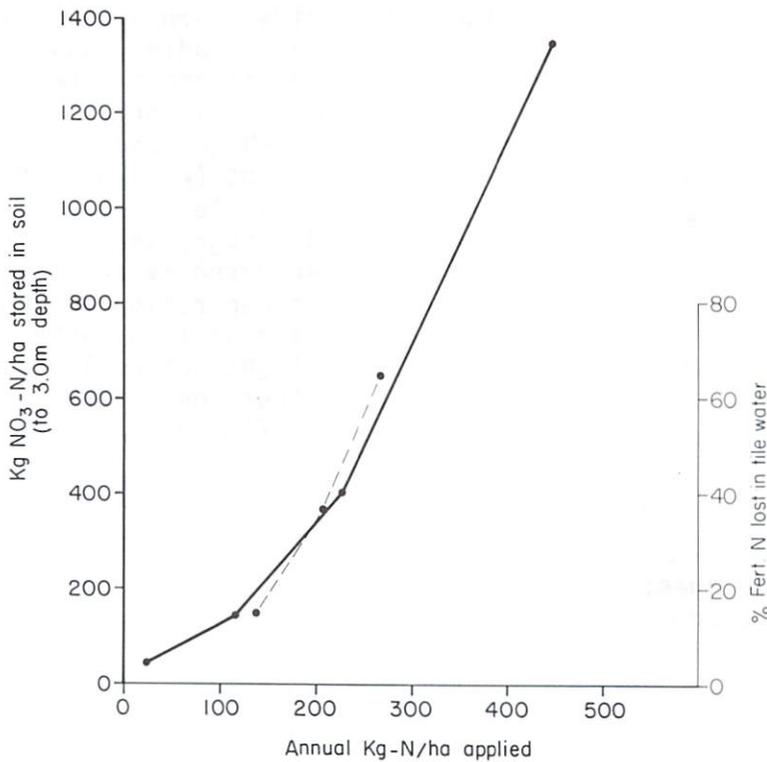


C. Iowa; Webster SiL; 5 year averages; Baker and Johnson, 1981; circled point, Kanwar et al., 1983.

Figure 41. Midwestern experiment farm studies showing relationship between N-fertilization rate (kg-N/ha) and the amount (kg-N/ha) of NO₃-N lost in tile-drainage, and the flow-weighted average NO₃ concentration in the tile-drainage water (light dashed lines). Other conventions as in figure 39.



D. Minnesota; Webster CL; 5 years treatment; Nelson and Randall, 1983.



E. Minnesota; Webster CL; 5 years treatment; Nelson and Randall, 1983; Buzicky et al., 1983.

Figure 41. Continued.

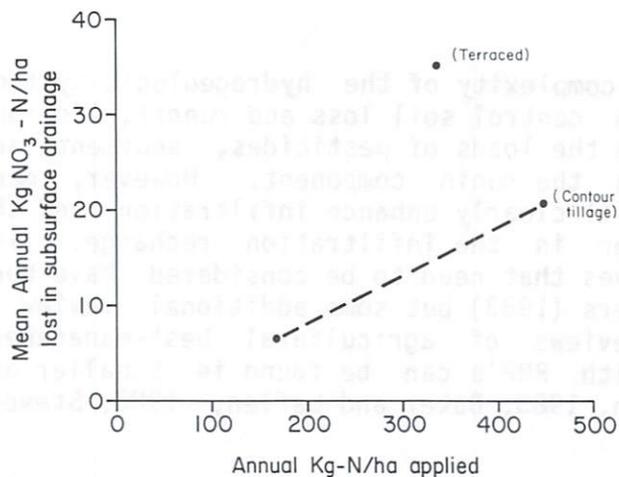


Figure 42. NO₃-N losses in subsurface seepage water: Iowa; Western Iowa Loess-soils; 5 years treatment; Burwell et al., 1976.

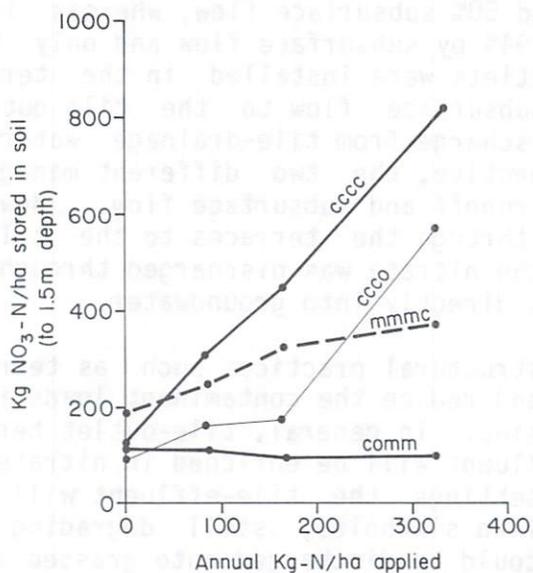


Figure 43. Relationships among N-fertilization rate, the amount of NO₃-N stored in the soil profile, and crop-rotations; Wisconsin; Rosetta SiL; 4 years rotation treatment; Olsen et al., 1970.

various alternatives because of the complexity of the hydrogeologic system. On the one hand, there is the need to control soil loss and runoff, to conserve the soil, as well as to reduce the loads of pesticides, sediment, and microbes, that enter groundwater in the runoff component. However, many standard approaches to this problem will clearly enhance infiltration and the delivery of chemicals to groundwater in the infiltration recharge. The broader scope of management alternatives that need to be considered have been briefly reviewed by Hallberg and others (1983) but some additional review is given below. (Recent pertinent reviews of agricultural best-management practices and the issues involved with BMP's can be found in Schaller and Bailey, eds., 1983; Baker and Johnson, 1983; Baker and Laflen, 1983; Stevenson, ed., 1982; Keeney, 1982).

Further Notes on Management Practices

Terracing agricultural land has been a widely used and effective tool for controlling runoff and soil erosion. As previously discussed studies of terraced vs. contoured corn showed that terracing enhanced infiltration and greatly increased nitrate leaching (figure 42). For comparable years, Burwell and others (1976) data show that the water-yield from the contoured watershed occurred as about 50% surface runoff and 50% subsurface flow, whereas in the terraced area the water-yield was about 94% by subsurface flow and only 6% by runoff. Subsequently, pipe or tile outlets were installed in the terraces which 'short-circuited' much of the subsurface flow to the tile outlets. Burwell and others (1976) lumped the discharge from tile-drainage water with their runoff component; in this perspective, the two different management systems produced similar proportions of runoff and subsurface flow. However, even the shorter subsurface flow path through the terraces to the tile enhanced nitrate leaching. Though now the nitrate was discharged through the tile-drainage water instead of to depth, directly into groundwater.

In the context of northeastern Iowa, structural practices such as terracing may be needed to control soil erosion, and reduce the contaminant loads in the runoff-recharge component in sinkhole basins. In general, tile-outlet terraces would be used, but as noted the tile-effluent will be enriched in nitrate (and other soluble chemicals). In such settings the tile-effluent will join surface-waters which will discharge into sinkholes, still degrading water quality. However, the tile effluents could be discharged onto grassed waterways; using grassed waterways and/or other riparian buffer strips along waterways and around sinkholes would likely slow down the delivery of water and chemicals to sinkholes, and allow further degradation and dissipation of chemicals and the uptake of nutrients (such as nitrogen) by the plants (Lowrance et al., 1984). Such combinations of practices (especially if combined with needed chemical management) may allow more integrated protection of soil resources with improvements in groundwater quality.

A variety of factors come into play in the realms of chemical and total agricultural management. Crop rotations can be important for soil-erosion control and even proper manure applications can help reduce runoff and soil loss (e.g., Mueller et al., 1984). The effects of rotation, of alfalfa in

particular in far northeastern Iowa, and manure must be considered in fertilizer management. Consideration of credits for the nutrients supplied from these sources, can lower chemical inputs and thus help reduce nitrate leaching (see figure 43 for example).

Some studies also show that some nitrate leaching can occur during, and particularly following, alfalfa crops and from the plowing (and subsequent mineralization) of 'grasslands,' or green manure crops. However, large NO_3 losses in these situations are generally associated with fallowing the land, addition of chemical fertilizer-N, and/or following the plowed grass or alfalfa with crops that are not high-rate nitrogen users (e.g., Cameron and Wild, 1984; Robbins and Carter, 1980). For example in a study in Idaho, leachate concentrations of nitrate under alfalfa reached values of 15 mg/l; under unfertilized corn after alfalfa they reached 31 mg/l; but under fertilized corn following alfalfa reached 64 mg/l. For the two years after the alfalfa the fertilized corn (fertilized at 170 and 200 kg-N/ha for the first and second year, respectively) lost an average of 92 kg NO_3 -N/ha more than the unfertilized corn, an equivalent of about 50% of the applied-N (Robbins and Carter, 1980).

As noted in the previous discussion fall applications of fertilizer-N in the Midwest can result in larger leaching losses, although weather and the type of fertilizer-N are important factors. Nitrate-N forms have shown greater gaseous losses and greater downward movement than fall-applied urea-N, even in the cool-dry climates of the Northern Great Plains (Aulakh and Rennie, 1984). In these cooler climates the major portion of the fall-applied N that was lost was related to denitrification (or at least gaseous losses) which occurred during the fall (before the soil froze) and at spring thaw; in the warmer, wetter Midwest these periods are when leaching losses would also likely occur. In the Canadian study N-stabilizers helped to reduce gaseous-N losses and delayed ammonium nitrification and downward movement of fertilizer-N in the soil. However, they did not affect the largest 'loss' of available-N; 15 to 25% of the fall-applied fertilizer-N was not available the following spring because it was biologically immobilized. The warmer and wetter climate of the Midwest favor greater likelihood of significant leaching losses of fall-applied N as noted by Nelson and MacGregor (1973), Olsen and others (1970), and Buzicky and others (1983). In the Midwest the largest gaseous losses occur at spring thaw and Goodroad and others (1984, p. 561) note this "may at least in part explain the often-observed inefficiency of fall-applied fertilizer N." The large increase in nitrates in groundwater in the Big Spring basin in November and December of 1982 (figure 2) may, in part be related to the warm, wet weather following fall application of fertilizer-N in the basin, although we would estimate that only a relatively small portion of the corn acreage received fall-N.

Further detailed work is needed on N-stabilizers or nitrification inhibitors in the Midwest, particularly with reduced amounts of fertilizer-N and/or multiple applications. Timmons (1984) found that over a 3-year period nitrification-inhibitors reduced leaching losses only 7%, with irrigated corn. However this was at a relatively high-rate of fertilization (224 kg-N/ha or 200 lbs-N/ac) and because the inhibitors did not carry over, large winter-spring leaching losses can occur. At these rates results were not consistent, since the inhibitors reduced NO_3 -N leaching during the growing season by 12 to 17% during 2 of the 3 years, and post-harvest leaching by 38% for one year.

No yield differences were observed because of the high rate of N-application. For perspective, the annual $\text{NO}_3\text{-N}$ leaching losses on these sandy, irrigated soils averaged about 160 kg-N/ha (143 lbs-N/ha) without nitrification-inhibitors, an equivalent of over 70% of the applied fertilizer-N. Further work is needed on the more typical silty and loamy soils of the Midwest, under natural rainfall and a broad range of N-rates.

Multiple applications of N or even timing application more closely to when the corn will use it, can help to reduce leaching losses and likely increase yields at the same time (e.g., Timmons and Dylla, 1981; Biegeriego et al. 1979; Arora and Juo, 1982).

As another aspect of N-management, research and extension work must continue to develop a means to more accurately predict N-fertilizer requirements, either through combination soil tests or perhaps even plant tissue testing (e.g., Fox and Piekielek, 1984; Rauschkolb et al., 1974). Recent work in Pennsylvania shows that some current methods recommend fertilizer-N applications more than 100 kg-N/ha (90 lbs-N/ac), greater than rates that would produce economic optimum production (Fox and Piekielek, 1984). Results of this study produced information that allowed more accurate recommendations that, if followed, would reduce N-fertilizer use by over 50 kg-N/ha (45 lbs-N/ha) in Pennsylvania, and still achieve (and be above) economic-optimum yields.

Conservation tillage and zero tillage ("no" till) are important practices for controlling soil erosion over extensive areas of the Midwest (e.g., Amemiya, 1977). However, there are mixed findings about the impact of conservation tillage on chemical management and water quality (e.g., Baker and Laflen, 1983).

There is no doubt that conservation tillage (or reduced tillage, RT) and zero tillage (ZT) reduce soil erosion relative to conventional tillage (CT) with a moldboard plow (see, for example, Amemiya, 1977; Moldenhauer et al., 1983; Angle et al., 1984; Cogo et al., 1984; Mueller et al., 1984). Several studies show that ZT reduces soil erosion by 75 to 90% (Baker and Johnson, 1983) compared to CT. Some forms of RT are somewhat less effective (Moldenhauer et al., 1983) and all practices are affected by rotation effects, particularly if soybeans are grown (e.g., Van Doren, et al., 1984; Cogo et al., 1984). RT and ZT are effective, in large part, because they leave some, or all of the former crop residues on the soil surface, and, in general, some studies suggest that soil erosion is an inverse, exponential function of the percentage of residue cover (Laflen and Colvin, 1981). This cover also helps conserve soil moisture which can improve crop yields in areas of moisture stress (e.g., Doran et al., 1984).

In part, the reduction in soil erosion occurs because RT and ZT generally reduce runoff as well (e.g., Onstad and Otterby, 1979; Moldenhauer et al., 1983; Baker and Johnson, 1983) particularly on a watershed basis (Angle et al., 1984). The reduction in runoff is highly variable though, and runoff from ZT is sometimes close to, or even greater than CT (e.g., Baker and Laffen, 1983; Mueller et al., 1984). The largest reductions in runoff are generally associated with RT, such as chisel-plow systems (Mueller et al., 1984; Baker and Laflen, 1983).

Reduction of soil loss is an important factor in improving surfacewater quality (and the quality of the runoff-recharge component in karst areas) but reductions in chemical losses in runoff water are not a direct function of the reduction in sediment loss and runoff water. Chemicals applied to the land may be lost via four pathways (see review by Baker and Laflen, 1983, as well): 1. in solution in subsurface drainage--the infiltration component; 2. in solution in surface runoff water; 3. in association with sediment (soil particles and/or organic matter) in the runoff water; or 4. in gaseous form to the atmosphere. Chemical losses in water or with sediment are related to both the volume of the water and sediment and the concentration of the chemical associated with them.

Several interactive factors contribute to the concentration of a chemical, and thus, the mass of the chemical that may be lost through these pathways. First, is the amount (or concentration) of the chemical and its distribution with depth within the soil. Second, is the chemical's persistence in the soil, or in other words, how long the chemical lasts before it is transformed into another compound or consumed by plants or other organisms. Third, is the nature of the reactivity of the chemical with the soil-mineral matter (e.g., clay particles), organic matter, and with the water itself (i.e., water solubility vs soil or organic matter adsorption). For example, naturally occurring organic-N will be lost with mineral-particulates in the runoff water that initiates soil erosion. Yet, with time some of this organic-N will mineralize, eventually to $\text{NO}_3\text{-N}$, which is highly soluble in water and anionic (i.e., it does not attach to soil or organic matter) and thus may be readily leached in infiltration water, if not taken up by plants as a nutrient. Most of the commonly used pesticides will breakdown to other compounds (over a period of weeks or months) if they remain in the very top of the soil profile. Some pesticides will bond very strongly to clay particles or organic matter and will primarily be lost with sediment. Many of the common herbicides are both moderately soluble and have only moderate affinities to attach to sediment. Thus, they tend to be lost both with runoff water and sediment. The distribution of a chemical within the soil profile is related to both its natural distribution (as with nutrients) and the amount added artificially and the mode of application as well. Chemicals that are applied to the soil surface and not incorporated have a higher probability of being lost with runoff. Those chemicals that are injected or incorporated and are soluble, have a greater chance of moving in infiltration.

For example, the concentrations and losses of atrazine in runoff water directly relate to the amount applied, as well as the timing of runoff events in relation to application (e.g., Hall et al., 1972; Triplett et al., 1978; Baker and Laflen, 1983; Hall et al., 1983; Glotfelty et al., 1984). The losses of atrazine in infiltration are more generally related to long term application rates, but concentrations and losses in infiltration are typically 10 to 100 times less than in runoff (e.g., Hall et al., 1983; Hallberg et al., 1983; Wehtje et al., 1984). Incorporation of atrazine may reduce losses in runoff by 25-70% (Baker and Laflen, 1979; Hall et al., 1983). In contrast, NO_3 is highly soluble and mobile and the greatest losses are with infiltration. Consequently, as noted, NO_3 losses in the infiltration component relate in nearly linear fashion to N-fertilization rates, at rates above 50 kg-N/ha.

This discussion sets the framework for review of the impacts of conservation tillage on water quality. Conservation tillage reduces the capability to

incorporate chemicals because, with present kinds of equipment, incorporation is accomplished mainly by tillage. Fertilizers or pesticides broadcast or sprayed on the soil surface are incorporated to about the same degree as crop residues for the different methods, and the objective of conservation tillage is to leave as much residue as possible. With ZT essentially no incorporation occurs. Many chemicals are applied on the residue/soil surface and rain must wash the chemicals into the soil. Particularly with the less mobile and soluble chemicals this results in a high degree of stratification in the soil profile, with very high concentrations occurring in the uppermost part (upper 50 mm) of the soil (Erbach, 1982; Baker and Laflen, 1983). The concentration of a chemical that is transported in runoff water is directly related to its concentration in the 'mixing-zone' in the uppermost 5-10 mm of the soil where this water and the soil interact (e.g., Ahuja and Lehman, 1983; Frere et al., 1980). Also, the reduction in concentrations of chemicals attached to sediment will not be directly proportional to the reduction in sediment loss because the chemicals are more often related to the finer, more chemically active (clays, colloids, and organic matter) portion of the sediment (Massey and Jackson, 1952; Baker and Laflen, 1983).

With the chemical stratification that develops under conservation tillage, the concentration of the more soluble nutrients (more soluble forms of N, P, K) in runoff water is generally greater from RT and ZT systems than CT, and in some instances even total soluble losses are greater (Romkens et al., 1973; Barisas et al., 1978; McDowell and McGregor, 1980). This is particularly true for the more soluble forms of P (Romkens and Nelson, 1974; McDowell and McGregor, 1980; Angle et al., 1984). However, the total losses of these nutrients in runoff water are still very low, generally less than 5 kg/ha (see Baker and Johnson, 1983).

Similarly, although RT and ZT systems reduce total soil loss in the runoff water the selective erosion and transport of finer-grained sediment from these systems causes an enrichment of sediment N and P (e.g., organic-N, various forms of available P and total P) in the sediment-phase of runoff losses, relative to CT (Massey and Jackson, 1952; Stoltenberg and White, 1953; Johnson and Baker, 1982). However, because the greatest loss of nutrients from runoff occurs with the sediment and because conservation tillage greatly reduces sediment loss compared to CT, the total nutrient loss in the the runoff component (water and sediment) is less with RT and ZT (Barisas et al., 1978; Angle et al., 1984).

Pesticide losses in runoff are complex and will commonly be related to the timing between application and runoff events in all tillage systems, but particularly in ZT. In ZT and some RT systems pesticides are applied directly on the crop residue. The most common herbicides do not interact with the residue and quickly wash off the residue (Martin et al., 1978). If the first rains after application are small, the pesticides may simply wash off the residue and infiltrate the soil into, or below, the mixing zone. However, if the first storm after application quickly generates runoff, large losses of pesticides may occur regardless of the tillage system (e.g. Glotfelty et al., 1984; Hall et al., 1983), but the effect can be more pronounced with ZT. Controlled rainfall simulation studies show that losses of commonly-used herbicides in runoff water increased directly with increases in residue cover, even though runoff volume and soil losses were less (Baker et al., 1978). However, in actual field studies the total losses of pesticides in runoff from NT and

RT systems have been less than from CT (Ritter et al., 1974; Baker and Johnson, 1979; Hall et al., 1984).

Other factors may relate to such losses as well. First, ZT systems in particular must depend on chemicals for pest control, particularly weeds. In other systems where primary (or mechanical) cultivation is used the amounts of pesticide used could be reduced. Second, herbicides applied onto crop residue may volatilize or degrade before rain washes them off. This will reduce their effectiveness and may necessitate additional post-emergence applications of herbicides, thus increasing the total amount applied. A third, and important factor, is the seasonal relationship of runoff from various tillage systems.

In the early crop-season (during tillage and shortly after planting) runoff generated from ZT is generally greater than from RT (such as chisel plowing) or CT (e.g., Mueller et al., 1984). This is because tillage (even RT) tends to loosen the soil, lowering its density (increasing the pore-space) and increasing surface roughness, all of which enhance infiltration, whereas in ZT the soil surface tends to be more dense, and more smooth, which will promote more runoff. As the growing season progresses, these differences decrease, because the soil surface in CT (and RT) systems become more compact simply from rainfall impact, shrinking and swelling, and other weathering processes which produce settlement, and possibly mechanical compaction from equipment. Thus, later in the season the runoff from ZT systems tends to be less than, or about equal to CT systems, and in most field studies RT systems, such as chisel-plow, actually show the least runoff and even the lowest soil losses on an annual basis (e.g., Mueller et al., 1984; Cogo et al., 1984; Baker and Laflen, 1983). Thus, early in the crop season during the critical period (within about 2-3 weeks of pesticide application) when the greatest losses of pesticides can occur, ZT systems may generate the greatest runoff and hence much higher concentrations and losses of pesticides in early season runoff water (e.g., Wauchope, 1978; Triplett et al., 1978; Hall et al., 1983).

It must be reiterated, however, that in field related studies, on an annual basis the lowest losses of total nutrients and total pesticides have come from ZT and RT systems. ZT and RT systems are invaluable tools to reduce soil erosion, and these points simply show, as reviewed by Baker and Laflen (1983) that there is still room to improve the effects on water quality from conservation tillage.

Review of the studies cited also show that new combinations of tillage and chemical application methods may provide these added benefits. Recent studies show that the greatest, total reduction in soil and water loss may come from systems that afford some incorporation of crop residues (e.g., Cogo et al., 1984; Mueller et al., 1984). Although the relationships are complex, this may suggest that pesticide incorporation, especially with new technological advances in equipment (e.g., Baker and Laflen, 1983, p. 192-193), might be accommodated with maximum soil loss reductions in RT systems. As noted, incorporation can dramatically reduce pesticide concentrations and total losses in runoff water. Incorporation might produce greater leaching losses, but, in perspective, runoff losses of pesticides can be in the realm of 1-10% of the applied pesticides, whereas leaching losses are typically much less than 1% (e.g., Hall et al., 1972; Hall, 1974; Triplett et al., 1978; Wauchope, 1978; Baker and Johnson, 1983; Hallberg et al., 1983, Hall et al., 1983; Wehtje et

al., 1984). Reducing peak concentrations in runoff would be of particular benefit in sinkhole basins; i.e., to lessen the transient high concentrations of pesticides that enter groundwater in the runoff component, as described earlier in this report. Further some recent work (Hall et al., 1983; for atrazine) suggests that incorporation might decrease the leaching losses of herbicides by enhancing the interaction with the soil, promoting greater adsorption on colloidal surfaces, and reducing the aqueous-phase mobility.

Hall and others (1983) also report that CT systems with corn and small grain strip-cropping and full incorporation of herbicides, reduced runoff, soil loss, and pesticide loss as effectively as RT systems. Again, it would seem apparent that RT systems that might afford chemical incorporation, combined with even narrow-base strip cropping, could be even more effective as a total conservation measure. Combinations of traditional methods, new technology, and chemical management can provide the holistic groundwater-surfacewater-soil resource conservation measures that will be needed.

Reduced Tillage Effects on Nitrogen Losses

There are a variety of mixed conclusions regarding N-losses from ZT and RT systems (see review in Rice and Smith, 1983). One area of confusion regards potential gaseous losses of N (primarily as N_2O). Gaseous losses result from both denitrification (under reducing conditions) and from the oxidation of NH_4 (Bremner and Blacker, 1978). Gaseous loss rates, and the dominant mechanisms involved, are related to the moisture regime-or soil water content, substrate availability (plant and microbe affects) (e.g., Mosier and Hutchinson, 1981; Rolston et al., 1982), possibly tillage and residue cover (Burford et al., 1981; Aulakh et al., 1982), and the rate and form of N-fertilization (e.g., McKenney et al., 1980; Breitenbeck et al., 1980; Bremner et al., 1981; Cochran et al., 1981; Seiler and Conrad, 1981; Aulakh and Rennie, 1984; Mulvaney and Kurtz, 1984). Total rates estimated also depend on the time of year measurements are made but emissions range from <1 to 16 kg-N/ha for rainfed agricultural systems (Bremner et al., 1980, 1981; Duxbury et al., 1982; Goodroad et al., 1984). Particularly in well-drained, rainfed agricultural systems the bulk of losses are related to the activity of NH_4 oxidizers, or nitrifiers (Breitenbeck et al., 1980; Bremner and Blackmer, 1981). The proportion of fertilizer-N evolved as N_2O in a cropping season is generally about 2% or less (e.g., Breitenbeck et al., 1980; Cochran et al., 1981; Goodroad et al., 1984).

Recent studies suggest that gaseous-N losses (from denitrification) from ZT systems may be greater than from CT because the population of microbial denitrifiers are greater while nitrifiers are 20-50% less in the upper 7.5 - 15cm (3-6 inches) of the soil in ZT, as compared to CT (e.g. Rice and Smith, 1982; Aulakh et al., 1984 a and b; Broder et al., 1984; Linn and Doran, 1984). However, Linn and Doran (1984) show that below the upper 7.5cm (3 inches) there is little difference in microbe populations and that denitrifier populations were actually somewhat greater in CT from 7.5 -15cm (3 to 6 inches). Aulakh and others (1984a and b) suggest that gaseous-N losses may be 5 -10 kg-N/ha/yr greater from ZT than CT, and that leaching losses may be 2-5% greater. Goodroad and others (1984) show gaseous-N loss rates under fertilized (200 kg-

N//ha) RT corn of 3.5 -6.3 kg-N₂O-N/ha as compared to background values of 1.0 -2.0 kg-N₂O-N/ha.

In contrast, El-Harris and others (1983) show that the soil N-mineralization potential of ZT and RT (chisel-plow) were greater than CT in the spring, but that by fall there was little difference. Carter and Rennie (1984) show that although there are short-term differences in mineralization and immobilization of N between tillage systems, there were no significant long-term differences. Similarly, Rice and Smith (1984) suggest greater short-term N-immobilization in ZT, but overall suggest that total differences in gaseous and leaching losses are not great.

Aulakh and others (1984a and b) suggest that the more dense surface soil and related greater moisture content in ZT are factors in promoting greater denitrification. As Rice and Smith (1983) note, the greater soil moisture, without water-logging (particularly in the better-drained soil environment) would also enhance nitrification. Several of these studies show that the normal additions of N-fertilizer make these microbial substrate differences ineffective and, in fact, promoted a 6-9 fold increase in the soil nitrifier population under all the tillage practices (Broder et al., 1984) promoting greater mineralization and nitrification (El-Harris et al., 1983; Rice and Smith, 1983). Rice and Smith (1983), using N-15 fertilizers noted that within 2 weeks of application 30% and 38% of the fertilizer-N were lost from the upper 15cm (6 inches) of the soil under CT and ZT respectively. Tyler and Thomas (1977), in a lysimeter study, note greater leaching losses of fertilizer-N from ZT than CT, with most of the losses occurring in the late spring and early summer (in large part by macropore flow) before the corn uptake was significant and when moisture contents in ZT were higher than CT.

In sum, these data suggest that ZT and RT systems may increase both gaseous and leaching losses of N, but that in large part these differences are related to N-fertilization, and the total difference in N-loss appears to be small, perhaps 2-10% more than with CT (e.g., Rice and Smith, 1983, 1984; Aulakh et al., 1984b; Tyler and Thomas, 1977). These differences are hardly significant, considering the other benefits of conservation tillage, i.e., the most important part of the problem is the first 30-80% equivalent of the fertilizer-N that is not being used by the crop, regardless of tillage system. And in fact some studies suggest greater crop uptake of N under ZT as well (Aulakh et al., 1984b; Rice and Smith, 1983).

Limited research available suggests that the effects of herbicides, particularly atrazine, on denitrification are minimal (e.g., Cervelli and Rolston, 1983; Goring and Laskowski, 1982) as are the effects of tillage on atrazine dissipation (Ghadiri et al., 1984). The long-term applications of N-fertilizers have contributed to soil acidity which have minimized the effect of tillage on atrazine dissipation (except in calcareous soils). Additional research on the effects of different tillage systems on N-losses and pesticides is needed.

Detailed research data are needed on many aspects of nitrogen and pesticide management. As noted, some reports suggest that the form of the fertilizer-N may affect the amount of gaseous losses and leaching losses and, in combination with corn-genotypes, even the crop-N uptake and grain production (e.g., Pan et al., 1984; Nelson and MacGregor, 1970). The large amounts of

fertilizer-N that are lost or unused clearly imply that if the N could be made more effective that large corn yields could be obtained with substantially reduced chemical-N inputs. With the larger amounts of N applied there are, as shown, larger amounts of N available for crop uptake but the yield responses over time and some isotope work suggest that soil-N use may also be enhanced through some form, albeit controversial, of a "priming" effect (Hauck and Bremner, 1976; Westerman and Kurtz, 1973; Olson and Swallow, 1984; Feigenbaum et al., 1984). These large N-losses clearly suggest that fertilizer-crop response models need reevaluation in terms of N-efficiency and actual N-uptake.

SUMMARY AND DISCUSSION

Water-year 1983, the second complete year of monitoring in the Big Spring basin, provides some interesting contrasts to the first year of study in the region. Significantly more detailed hydrologic and water-chemical monitoring were done for particular hydrologic events, to provide further understanding of (karst) carbonate aquifer systems, in general, and the Big Spring hydrologic system, specifically.

Overview WY-1983

There was a dramatic change in land management in the basin because of the PIK program. Reduction in total corn acreage and slight reductions in fertilization rates produced about a 30-40% decrease in N-fertilizer application for the basin, and a somewhat lesser decrease in pesticide use. However, WY-1983 had considerably greater precipitation than WY-1982; increasing from about 34 inches (864 mm) in 1982 to about 44.5 inches (1,130 mm) in 1983 an increase of 31%. The increase was mainly related to abundant rainfall in late-fall and early winter (November-December, 1982) and summer (late June - early July, 1983). The total range of (instantaneous) discharges measured at Big Spring, from 32 to 295 cfs (0.9 - 8.4 cms) was nearly identical for the two years.

The greater precipitation increased the total water discharged from the basin by about 47% over WY-1982; surfacewater discharge increased 100% and groundwater discharge (disregarding WY-1982 storage changes) increased 37%. The total water-yield equalled about 49% of precipitation. For groundwater, the runoff, conduit-flow component increased 34% while the infiltration, base-flow component increased 8% (WY-1982 storage effects cannot be removed from this figure). Even with the greater discharge these groundwater components still occur in the same relative balance over the course of a water-year, with the runoff, conduit-flow component comprising only 11% of the groundwater discharge, while the infiltration component comprises 89% of the discharge.

The greater water discharge, and particularly the greater groundwater movement through the soil in infiltration caused a significant increase in chemical discharge from the basin. Total nitrate-N discharged from the basin in WY-1983 increased 58% from WY-1982, and totalled more than 1,430 tons (13×10^5 kg) of N; approximately 755 tons (6.9×10^5 kg) in groundwater, and 675 tons (6.1×10^5 kg) in stream-flow. This equals about 43 lbs-N/ac (49 kg-N/ha) for the entire basin. The flow-weighted mean nitrate concentration in groundwater increased from 39 mg/l in WY-1982 to 46 mg/l in WY-1983. Thus, the mean nitrate concentration for the basin exceeded the the 45 mg/l drinking water standard.

Similar trends were recorded on the regional basis as well. The discharge of the Turkey River at Garber increased 40% from WY-1982, and nitrate-N losses also increased substantially. The total $\text{NO}_3\text{-N}$ discharged from the Turkey River basin was approximately 13,400 tons-N (12.1×10^6 kg-N) (up from 9,400 tons of N in WY-1982) an equivalent of 27 lbs-N/ac (30 kg-N/ha) for the entire

region.

The discharge of pesticides with water from the basin also increased substantially in WY-1983, particularly in groundwater. The discharge of the herbicide atrazine in groundwater increased 120% over WY-1982. However, this still only amounted to about 31 lbs (14 kg) of atrazine. Atrazine was the only pesticide detected in groundwater year-round, with concentrations ranging from 0.1 to 5.1 $\mu\text{g/l}$, with a flow-weighted mean of 0.28 $\mu\text{g/l}$. Four other commonly used herbicides were intermittently detected in groundwater, but principally during runin-recharge events in May, June, and July. These herbicides were (maximum concentrations noted in parantheses, before common name): Lasso (0.63 $\mu\text{g/l}$, alachlor); Bladex (1.2 $\mu\text{g/l}$, cyanazine); and Dual (0.62 $\mu\text{g/l}$, metolachlor). Lasso appeared in groundwater as late as 8/30/83. The insecticide Dyfonate (fonofos) also appeared in groundwater (0.11 $\mu\text{g/l}$) during the large runin-recharge, storm event of late-June, early-July 1983. Even though the amount and concentration of pesticides in water increased substantially in WY-1983, the total mass discharged is still estimated at only about 5% of that normally applied. Numerous other pesticides that were applied in the basin were not detected in groundwater.

Large spring or early summer runoff and discharge events can significantly affect the total pesticides lost in water. During the two week period of large runoff-discharge events in late-June and early-July about 35% of the total WY-1983 discharge of atrazine occurred. The amount discharged during this period alone equaled about 80% of the atrazine discharged in WY-1982.

Components of Groundwater and Chemical Discharge

As noted, the contributions of the components of the groundwater discharge were approximately the same in WY-1983 as in WY-1982; the infiltration, base-flow component comprising about 90% of the water discharge, and the runin, conduit-flow component only 10%. The highest concentrations and largest mass of nitrate are delivered through the infiltration-component (95%) while the runin-component delivered only 5% of the nitrate-N. This delivery was similar to WY-1982. With the large runoff-runin events during WY-1983 the relative delivery of pesticides (based on atrazine) to groundwater was substantially different. In WY-1983 the runin component delivered 47% of the pesticides, with a flow-weighted mean atrazine concentration of 1.2 $\mu\text{g/l}$, while the infiltration component delivered 53% of the pesticides, with a flow-weighted mean atrazine concentration of only 0.16 $\mu\text{g/l}$. In WY-1982 the relative delivery of pesticides was 16% for runin, and 84% for infiltration. Even with the different conditions of WY-1983 the infiltration component still delivers the largest mass of contaminants into the groundwater system. These findings are supported by research in Floyd and Mitchell counties, as well (Libra et al, 1984). The respective contributions of these components must be considered in any planning of remedial measures or management practices.

Nitrate Fluctuations and the Hydrogeologic System

Nitrate concentrations monitored from tile-lines, surfacewater sites, Big Spring and the Turkey River all fluctuate in harmony throughout the years of monitoring. The parallel nature of the records demonstrate that similar mechanisms and responses to recharge deliver nitrate to all parts of the hydrologic system. The close coincidence of both nitrate and discharge records between Big Spring and the Turkey River show that the processes and relationships documented at Big Spring are applicable on the regional scale as well.

NO₃-N Losses and Landuse

The total NO₃-N losses from the Big Spring basin increased from an equivalent of 27 lbs-N/ac (31 kg-N/ha) in WY-1982 to 43 lbs-N/ac (49 kg-N/ha) in WY-1983. Obviously, there is no direct relationship between the NO₃-N discharged and the decreased application of fertilizer-N which resulted from the PIK program in calendar year 1983. This is because of the time lag between changes in chemical land-treatment and changes in the chemical quality of the groundwater (combined with differences between crop, or calendar years and water-years). As shown by a review of various agronomic studies, at moderate to high N-fertilization rates NO₃-N is stored in the soil, and the amount builds up in direct proportion to the amounts applied and the number of years of application. The NO₃-N leached in any year, such as WY-1983, is in large part, related to this storage, which masks the effects of individual years in the short term. Any impact, or decrease in NO₃-N leaching resulting from PIK, would be expected to show in future monitoring. Landuse in the Big Spring basin has been relatively constant between 1979 and 1983, and thus the NO₃-N losses can be put in the context of the acreage that has been in corn production over that time (3-5 years in various rotations). In this perspective the amount of N lost from this acreage base increased from 47 lbs-N/ac (52 kg-N/ha) in WY-1982 to 74 lbs-N/ac (83 kg-N/ha) in WY 1983. Again for perspective the WY-1982 N-losses were equivalent to 33% of the fertilizer-N applied in 1982; the WY-1983 N-losses would be equivalent to 53% of those same 1982 N-fertilizer amounts. Note that this is a minimum figure because it only accounts for NO₃-N losses. Thus, in a relatively wet year, such as WY-1983, a minimum equivalent to about 50% of the chemical fertilizer-N applied may be lost into groundwater and surfacewater combined. Particularly considering how well the behavior in the Big Spring system reflects regional conditions, the magnitude of N-losses would certainly seem to constitute an economic as well as an environmental loss.

As noted these figures are minimums for the amount of N lost from the basin. Piezometer studies and stream monitoring in the basin show that denitrification occurs in local-settings in the soil environment, and possibly in the streams themselves, accounting for additional lost N, that cannot be quantified. Monitoring of ammonium-N and organic-N show that these forms of N are also discharged in groundwater during runin-recharge events. They are

discharged in higher quantities in streamflow which leaves the basin. In total they may constitute 10% additional to the N lost from the basin.

Suspended Sediment in Groundwater

In the unique karst-carbonate aquifer system suspended-sediment also occurs in groundwater causing water-quality problems, particularly during runoff, conduit flow periods. During base flow, suspended sediment concentrations at Big Spring are negligible, but during peak, conduit-flow the sediment loads are essentially equal to surface-runoff water, reaching concentrations of nearly 5,000 mg/l and discharge rates of over 190,000 lbs/hr (87,000 kg/hr). The total discharge of suspended sediment at Big Spring alone was about 3,500 tons (3.2×10^6 kg). These sediment loads create serious problems for the ICC fish hatchery operations.

In addition, to the water-quality problems turbidity and mineral-sediment create, the suspended-sediment load also introduces a variety of organic material into the aquifer, ranging from microbes to whole corn stalks, that can be seen discharging at Big Spring. Pesticides also occur attached to mineral or organic matter particles.

Detailed Monitoring of Discharge Events

Detailed monitoring of discharge and water chemistry, dye tracing, and hydrograph analysis of major discharge events during WY-1983 provide many insights to the behavior of the karst-hydrogeologic system. These data verify, and amplify, the prior findings (Hallberg et al., 1983) about the flow system and the nature of the contributing components.

While the recharge-discharge mechanisms are complex, different analytical and chemical hydrograph separation techniques show that the two fundamental components--infiltration base-flow, and runoff conduit-flow--can be consistently quantified within about 10%. The chemical monitoring and separation techniques also verify the complexity of components which contribute to major discharge-hydrograph events, and contribute to the nature of water-quality fluctuations.

Monitoring of rainfall-runoff events shows that the high surfacewater concentrations of parameters such as suspended sediment (e.g., 5,000 mg/l), pesticides (5-20 μ g/l), organic and ammonium-N move through the conduit-groundwater system as a 'slug' discharging from the groundwater in essentially the same concentration as they entered. These events also introduce bacteria and potentially pathogenic organisms into groundwater. While the runoff component delivers contaminants to the groundwater which are of concern for public health on the local level, the infiltration component is responsible for regional aquifer contamination. Also, infiltration is the recharge

mechanism common to all aquifers, which gives these data much broader implications.

Detailed monitoring shows that the relationships between rainfall-runoff in the basin and the time to response at Big Spring are complex, and vary with the antecedent conditions. When runoff, conduit-flow, discharge events occur during low-discharge, base-flow periods the timing between runoff, within the basin, and the 'rise' in discharge at Big Spring, appears to be inversely related to the magnitude of the event, particularly when a succession of events occur and each successive event is larger than the previous one. Smaller events initiate a rise in Big Spring discharge within 12-24 hours after runoff, but successive larger events take longer. Events which have exceeded 200 cfs (5.7 cms) at Big Spring have response times between 24 and 36 hours. Runoff-water from sinkholes on the west-side of the basin arrives at Big Spring within 12-24 hours, but the maximum water-quality changes indicating 'new-water' from runoff (from the basin as a whole) generally arrives at Big Spring between 36 and 40 hours after runoff (up to 48-54 hours after runoff for the successively larger events).

When discharge peaks are generated by snowmelt (and/or runoff) when the spring is discharging at 85 cfs (2.4 cms) or greater the rise begins within about 9 hours, suggesting that at these higher discharge rates the head in the aquifer is high enough, and the conduits are filled with enough water, that the additional recharge causes a head increase that can be more rapidly transmitted as a pressure-wave. Even under these conditions the change in water quality that marks the arrival of this 'new' runoff, conduit-flow water does not occur until 21-24 hours after runoff.

Large hydrologic events that promote either elevated base-flow, or the initiation of peak-flow recession at discharges greater than about 85 cfs (2.4 cms) generated some unique water-quality changes in the groundwater. For purposes of discussion we have termed these phenomenon nitrate 'plateaus', from the overall shape of the plot of nitrate concentrations with time. The plot of nitrate concentrations for these plateaus is marked by: 1. a sharp rising limb, in which nitrate concentrations abruptly increase about 50% (e.g., from about 50 up to 75 mg/l) in less than 24 hours; 2. a relatively stable, flat-topped portion (at the high-concentration level) which lasts for 5 to 7 days; and 3. a sharp termination, during which nitrate concentrations fall 25-50% (e.g., from 75 to 50 mg/l) in less than 24 hours; and then 4. more gradually recess until the next event. Observations show that these plateaus mark a unique phenomenon which is related to the overall infiltration, diffuse-flow component. The plateaus are not related to any discrete parcel of water. The rising limb can be explained as the relatively rapid passage of runoff, conduit-flow water (dilute in nitrate) followed by new infiltration-water, enriched in nitrate which is displaced from "storage" in the soil profile. The falling limb, or termination, is more difficult to explain. The terminations occur during gradual discharge recession and seem to indicate that the decline in head, during recession, lowers the water table below the zones of high nitrate concentrations in the soil in the high infiltration portions of the basin. The continued gravity drainage, infiltration-recharge, subsequently comes from lower in the soil-rock system from zones containing lower nitrate concentrations.

The monitoring of tile-drainage water has helped provide insights into the

plateaus, as well as providing other proxy observations of the behavior and quality of the shallow groundwater in the basin. Of note also, is that the pesticide concentrations noted in the tile-lines are essentially the same as those in the deeper groundwater. This suggests that once pesticides have leached out of the topsoil environment through the 2-5 feet of soil (0.6-1.6m) above the tile-lines, that little additional degradation takes place during further movement through the soil or in groundwater.

Soil Nitrates

Numerous soil cores were collected from the basin, to varying depths (2 -30 feet), under various landuse, after corn-harvest in 1982 and 1983. The soil samples were analyzed for $\text{NO}_3\text{-N}$ and pesticides. The $\text{NO}_3\text{-N}$ data were summarized into lb/ac (and kg/ha) equivalents by depth. The amount of $\text{NO}_3\text{-N}$ stored in the profile vary directly with landuse and increased proportionately with the number of years of fertilized corn. These results are in direct agreement with many other agronomic studies, and again show the inter-relationship between N-fertilization and NO_3 leaching to groundwater. Measured to a depth of 10 feet (3 m) the amount of $\text{NO}_3\text{-N}$ stored in soils under forest, pasture, fertilized-pasture and alfalfa-meadow (in 5 yr. rotation with corn) ranged from 48-80 lbs-N/ac (50-90 kg-N/ha) while under high fertilization (150-175 lbs-N/ac) corn the amounts ranged from 135 lbs-N/ac (150kg-N/ha) under second-year corn to 400 lbs-N/ac (450 kg-N/ha) under 'continuous' corn.

Soil Pesticides

The same (fall, post-harvest) soil cores were analyzed for pesticide residues. In the plow-layer maximum concentrations of 120.0 $\mu\text{g/kg}$ atrazine, 5.8 $\mu\text{g/kg}$ Bladex (cyanazine), 23.0 $\mu\text{g/kg}$ Lasso (alachlor) and 10.0 $\mu\text{g/kg}$ Dyfonate (fonofos) were recorded. Atrazine concentrations of 1.0 $\mu\text{g/kg}$ were noted at depths of nearly 10 feet (3.0 m), and 0.3 $\mu\text{g/kg}$ atrazine were detected at a depth of 14.5 feet (4.4 m) at one location. Other pesticides were not detected at great depths. These data illustrate that the herbicide atrazine, at least, is leaching to substantial depth through the loessial materials. These concentrations at depth are very similar to the atrazine concentrations that persist in groundwater year-round in the basin.

Atrazine is the only pesticide that has been detected in groundwater year-round in the Big Spring basin. It is also the most widely used herbicide in the basin and has been used widely for a longer period of time than the other herbicides. Atrazine has been in use in the area for over a decade.

Bladex, Lasso, and Dual have only been detected intermittently in the groundwater, generally in relation to runoff-recharge events in May through August. In general, atrazine has a lower water-solubility than these other common

herbicides. However, at the low-concentrations they are occurring their total solubility is not a major factor. Bladex, Lasso, and Dual (and Sencor/Lexone-metribuzin) have been detected year-round in groundwater in Floyd and Mitchell County (Libra et al., 1984). These herbicides are used more extensively, relative to atrazine, in the Floyd-Mitchell area because of the common rotation of soybeans with the corn. Thus, total use (and length of time used) in these areas may be a key factor in the appearance and persistence of these herbicides in the groundwater system.

Persistence in the soil is another key factor. Atrazine is not used on land in rotation with soybeans because it is noted for "carryover" problems. In general, in most common guides the soil persistence of atrazine is listed as 8-32 weeks, whereas the persistence of other three are commonly cited as 4-12 weeks. The persistence and carryover of atrazine is well documented in various studies (e.g., Armstrong et al., 1967; Roeth et al., 1969; Burnside et al., 1971; Burnside and Wicks, 1980; Frank et al., 1982; Jones et al., 1982), but the 'half-life' is estimated variously from 37 days (Dao et al., 1979) to 3 to 5 years (Armstrong et al., 1967). Recent, well documented studies show a half-life in the soil environment of about one year (Jones et al., 1982), whereas in estuarine water and submerged sediment it was about 1-2, and 2-3 weeks, respectively. Atrazine degradation increases with soil acidity (Armstrong et al., 1967) and it is much more persistent in the relatively alkaline, montmorillonitic soils of the midwest than the more acid, kaolinitic soils of the southeast (Best and Weber, 1974) and has generally been found to be the most persistent herbicide used in the midwest (e.g., Burnside and Schultz, 1978). Most of this research has concentrated on the fate or persistence of atrazine in the plow layer and little is known about the persistence of atrazine below this. Roeth and others (1969) and Harris and others (1969) show that degradation in the subsoil proceeds at about one-third the rate as in the plow-layer, even though some studies suggest non-biological hydrolysis is the primary means of degradation (e.g., Ghadiri et al., 1984). In field studies where Lasso (alachlor) was applied in larger quantities than atrazine, atrazine still occurred more persistently and at higher concentrations in runoff and subsurface flow water (Wu et al., 1983).

The leaching of atrazine through the soil into deep tile drains and groundwater base flow to streams has been widely noted, as well as its year-round persistence in these groundwater environments (Burnside et al., 1971; Muir and Baker, 1976; Von Stryk and Botton, 1977; Schwab et al., 1973; Frank et al., 1982; Wu et al., 1983; Wehtje et al., 1984). These studies report concentrations in the same range as noted in Iowa, except Schwab and others (1973) who report weighted-average concentrations in tile-effluent as great as 174 $\mu\text{g/l}$, under conditions of unusually high application and irrigation.

The leaching of atrazine through at least 16 feet (5 m) of sandy soil, and into groundwater, has been well documented in Nebraska (Spalding et al., 1980; Junk et al., 1980; Wehtje et al., 1984). In these irrigated alluvial aquifers in Nebraska atrazine also persists year-round and fluctuates seasonally in concentration generally reaching maximum levels of about 3.0 $\mu\text{g/l}$ (but locally up to 8.3 $\mu\text{g/l}$ in a very shallow research well; Wehtje et al., 1983). Wehtje and others (1984) show that direct downward leaching is the cause of the low-level atrazine contamination in the groundwater. The aquifer here is also contaminated with nitrates from the leaching of N-fertilizers (Linderman et al., 1976). They found that the atrazine being delivered to groundwater, at

any particular time, was residual atrazine in the soil profile related to the buildup and leaching over a number of years of application. The seasonal fluctuations in concentration showed that the atrazine was delivered to groundwater in "pulses" or "waves" of greater and lesser concentration. This is likely related to differential leaching, and redistribution in the soil, and differential partitioning between soil adsorbed and solute phases under different degrees (and time) of saturation. In another study Wehtje and others (1983), studied the fate of atrazine under aquifer conditions and found no evidence of microbial degradation, but found that limited degradation by hydrolysis occurred. Enough atrazine dissipation occurred in the aquifer (through adsorption, dispersion, and degradation) that they concluded that the yearly-average value of 0.38 $\mu\text{g/l}$ atrazine in the aquifer probably represented a steady-state condition between the amount annually delivered and the amount degraded and dissipated in the aquifer. However, not all of their water-sample data support this.

All of these various studies (and previously cited studies) support the findings of the authors' studies in the Big Spring basin and the Floyd-Mitchell county area. Commonly-used herbicides in particular can leach into, and persist in the subsoil, and leach directly into groundwater. The concentrations in groundwater will likely relate to amounts applied and duration or history of application, the efficiency of leaching, as well as the chemicals persistence. Once in the groundwater, concentrations may decline between major influx periods because of dispersion and degradation; though degradation will likely be limited under aquifer conditions. Atrazine concentrations in winter-spring groundwater base-flow in the Big Spring basin tended to be slightly higher in late 1983 than late 1982, but there is not enough record to suggest that this has significance; it may simply relate to the greater recharge during WY-1983.

Temporal Changes in Water-Quality

Other water-quality and crop-use data collected in the region (see Hallberg et al., 1984) further support the direct, linear relationship, between the increase in nitrates in groundwater with the large increase in N-fertilization that has taken place since the 1960s. A review of agronomic studies which have related N-fertilizer application rates to the N-buildup in soils or the N-losses in tile drainage, show that this linear relationship is precisely the response that should be predicted in a setting such as northeastern Iowa.

On the short term, seasonal or monthly basis, the concentration of NO_3 and mass of $\text{NO}_3\text{-N}$ discharged show significant, positive, linear relations to the amount of water discharged. Over the long term the excess $\text{NO}_3\text{-N}$ is stored in the soil. Because infiltration through the soil is the principle component of recharge, the timing of nitrate fluctuations in water supplies is related to seasonal recharge periods, and generally not to the timing of seasonal agricultural practices.

The direct relationships between total fertilizer-N applications and groundwater nitrate concentrations also indicate that any significant decrease in the amounts of fertilizer-N applied (or increased efficiency of N-use, such

that less could be leached) would be accompanied by a proportional decrease in groundwater nitrate, at least when integrated over a 2-5 year period.

Review of Agricultural Management Practices and Water-Quality

Management alternatives, or 'best-management practices' (BMPs), need to be formulated that will couple standard concerns for soil erosion and surface-water quality with the need to reduce chemical losses in infiltration to groundwater. This will need to be done to balance our need for efficient agricultural production with the need for safe drinking water. Some measures, such as terracing will control soil erosion and runoff but will promote greater infiltration and additional chemical leaching. Over time these problems can be addressed through new technology; improved equipment, chemicals, and plant-breeding. However, a review of many studies suggests that through new combinations of many current and accepted practices these goals can be compatible. Better chemical and nutrient management must be coupled with systems for soil management, as well.

REFERENCES CITED

- Adriano, D. C., Pratt, P. F., and Bishop, S. E., 1971, Nitrate and salt in soils and groundwaters from land disposal of dairy manure: *Soil Sci. Soc. Am. Proc.*, v. 35, p. 759-762.
- Ahuja, L. R., and Lehman, O. R., 1983, The extent and nature of rainfall-soil interaction in the release of soluble chemicals in runoff: *Jour. Environ. Qual.*, v. 12, p. 34-40.
- Amemiya, M., 1977, Conservation tillage in the western corn belt: *Jour. Soil and Water Conserv.*, v. 32, no. 1, p. 29-36.
- Angle, J. S., McClung, G., McIntosh, M. S., Thomas, P. M., and Wolf, D. C., 1984, Nutrient losses in runoff from conventional and no-till corn watersheds: *Jour. Environ. Qual.*, v. 13, p. 431-435.
- Armstrong, D. E., Chesters, C., and Harris, R. F., 1967, Atrazine hydrolysis in soil: *Soil Sci. Soc. Am. Proc.*, v. 31, p. 61-66.
- Arora, Yagesh, and Juo, A. S. R., 1982, Leaching of fertilizer ions in a kaolinitic ultisol in the high rainfall tropics: leaching of nitrate in field plots under cropping and bare fallows: *Soil Sci. Soc. Am. Jour.*, v. 46, p. 1212-1218.
- Aubertin, G. M., 1971, Nature and extent of macropores in forest soils and their influence on subsurface water movement: *U.S.D.A. For. Serv. Res. Paper NE-192* (Northeast. For. Exp. Stn., Upper Darby, PA.), 33p.
- Aulakh, M. S., and Rennie, D. A., 1984, Transformations of fall-applied nitrogen-15-labelled fertilizers: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 1184-1189.
- Aulakh, M. S., Rennie, D. A., and Paul, E. A., 1982, Gaseous nitrogen losses from cropped and summer-fallowed soils: *Can. Jour. Soil Sci.*, v. 62, p. 187-195.
- Aulakh, M. S., Rennie, D. A., and Paul, E. A., 1984a, Gaseous nitrogen losses from soils under zero-till as compared with conventional till management system: *Jour. Environ. Qual.*, v. 13, p. 130-136.
- Aulakh, M. S., Rennie, D. A., and Paul, E. A., 1984b, The influence of plant residues on denitrification rates in conventional and zero tilled soils: *Soil. Sci. Soc. Am. Jour.*, v. 48, p. 790-794.
- Baker, J. L., and Austin, T. A., 1982, Impact of agricultural drainage wells on groundwater quality: U.S. Env. Prot. Agency, Contract Rept., EPA Rept. No. G007228010, 126 p.
- Baker, J. L., and Johnson, H. P., 1977, Impact of subsurface drainage on water quality: *Proc. Third Nat'l. Drainage Symp.*, Am. Soc. Ag. Eng., St. Joseph, MO.

- Baker, J. L., and Johnson, H. P., 1979, The effect of tillage systems on pesticides in runoff from small watersheds: *Trans. Am. Soc. Ag. Eng.*, v. 22, p. 554-559.
- Baker, J. L., and Johnson, H. P., 1981, Nitrate-nitrogen in tile drainage as affected by fertilization: *Jour. Environ. Qual.*, v. 10, p. 519-522.
- Baker, J. L., and Johnson, H. P., 1983, Evaluating the effectiveness of BMPs from field studies; In Schaller and Bailey, eds., *Agricultural Management and Water Quality*, p. 281-304.
- Baker, J. L., and Laflen, J. M., 1979, Runoff losses of surface-applied herbicides as affected by wheel tracks and incorporation: *Jour. Environ. Qual.*, v. 8, p. 602-607.
- Baker, J. L., and Laflen, J. M., 1983, Water quality consequences of conservation tillage: *Jour. Soil and Water Conserv.*, v. 38, p. 186-193.
- Baker, J. L., Campbell, K. L., Johnson, H. P., and Hanway, J. J., 1975, Nitrate phosphorus, and sulfate in subsurface drainage water: *Jour. Environ. Qual.*, v. 4, p. 406-412.
- Baker, J. L., Johnson, H. P., Borcharding, M. A., and Payne, W. R., 1978, Nutrient and pesticide movement from field to stream: a field study; In Loehr, R. C., Haitn, D. A., Walter, M. F., and Martin, C. S., eds.: *Best Management Practices for Agriculture and Silviculture*, Ann Arbor Science Publishers, Inc., Ann Arbor, MI, p. 213-246.
- Barisas, S. G., Baker, J. L., Johnson, H. P., and Laflen, J. M., 1978, Effect of tillage systems on runoff losses of nutrients, a rainfall simulation study: *Trans. Am. Soc. Ag. Eng.*, v. 21, p. 893-897.
- Bassett, J., 1976, Hydrology and geochemistry of the Upper Lost River drainage basin, Indiana: *Nat. Speleological Soc. Bull.*, v. 38, #4, p. 79-87.
- Best, J. A., and Weber, J. B., 1974, Disappearance of s-triazines as affected by soil pH using a balance-sheet approach: *Weed Sci.*, v. 22, p. 364-373.
- Bigeriego, Manuel, Hauck, R. D., and Olson, R. A., 1979, Uptake, translocation, and utilization of ¹⁵N-depleted fertilizer in irrigated corn: *Soil Sci. Soc. Am. Jour.*, v. 43, p. 528-533.
- Breitenbeck, G. A., Blackmer, A. M., and Bremner, J. M., 1980, Effects of different nitrogen fertilizers on emission of nitrous oxide from soil: *Geophys. Res. Lett.*, v. 7, p. 85-88.
- Bremner, J. M., and Blackmer, A. M., 1978, Nitrous oxide: emission from soils during nitrification of fertilizer nitrogen: *Science*, v. 199, p. 295-296.
- Bremner, J. M., and Blackmer, A. M., 1981, Terrestrial nitrification as a source of atmospheric nitrous oxide. p. 151-170. In Delwiche, C. C., ed.: *Denitrification, nitrification, and nitrous oxide*. John Wiley, New York.

- Bremner, J. M., Breitenbeck, G. A., and Blackmer, A. M., 1981, Effect of anhydrous ammonia fertilization on emissions of nitrous oxide from soils: *Jour. Environ. Qual.*, v. 10, p. 77-80.
- Bremner, J. M., Robbins, S. G., and Blackmer, A. M., 1980, Seasonal variability in emission of nitrous oxide from soil: *Geophys. Res. Lett.*, v. 7, p. 641-644.
- Broder, M. W., Doran, J. W., Peterson, G. A., and Fenster, C. R., 1984, Fallow tillage influence on spring populations of soil nitrifiers, denitrifiers, and available nitrogen: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 1060-1067.
- Burford, J. R., Dowdell, R. J., and Crees, R., 1981, Emission of nitrous oxide to atmosphere from direct-drilled and ploughed clay soils: *Jour. Sci. Food Agric.*, v. 32, p. 219-223.
- Burnside, O. C., Fenster, C. R., and Wicks, G. A., 1971, Soil persistence of repeated annual applications of atrazine: *Weed Sci.*, v. 19, p. 290-293.
- Burnside, O. C., and Schultz, M. E., 1978, Soil persistence of herbicides for corn, sorghum, and soybeans during the year of application: *Weed Sci.*, v. 26, p. 108-115.
- Burnside, O. C., and Wicks, G. A., 1980, Atrazine carryover in soil on a reduced tillage crop production system: *Weed Sci.*, v. 28, p. 661-666.
- Burwell, R. E., Schuman, G. E., Saxton, K. E., and Heinemann, H. E., 1976, Nitrogen in subsurface drainage from agricultural watersheds: *Jour. Environ. Qual.*, v. 5, p. 325-329.
- Buzicky, G. C., Randall, G. W., Hauck, R. D., and Caldwell, A. C., 1983, Fertilizer N losses from a tile drained mollisol as influenced by rate and time of 15-N depleted fertilizer application: *Agron. Abstracts*, Am. Soc. Agron., Wash. D.C., p. 213.
- Cameron, D. R., Kowalenko, C. G., and Campbell, C. A., 1979, Factors affecting nitrate nitrogen and chloride leaching variability in a field plot: *Soil Sci. Soc. Am. Jour.*, v. 43, p. 455-460.
- Cameron, K. C., and Wild, A., 1984, Potential aquifer pollution from nitrate leaching following the plowing of temporary grasslands: *Jour. Environ. Qual.*, v. 13, p. 274-278.
- Carter, M. R., and Rennie, D. A., 1984, Nitrogen transformations under zero and shallow tillage: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 1077-1081.
- Cervelli, S., and Rolston, D. E., 1983, Influence of atrazine on denitrification in soil columns: *Jour. Environ. Qual.*, v. 12, p. 482-486.
- Chichester, F. W., and Smith, S. J., 1978, Disposition of ¹⁵N-labeled fertilizer nitrate applied during corn culture in field lysimeters: *Jour. Environ. Qual.*, v. 7, p. 227-233.

- Cochran, V. L., Elliot, L. F., and Papendick, R. I., 1981, Nitrous oxide emissions from a fallow field fertilized with anhydrous ammonia: *Soil Sci. Soc. Am. Jour.*, v. 45, p. 307-310.
- Cogo, N. P., Moldenhauer, W. C., and Foster, G. R., 1984, Soil loss reductions from conservation tillage practices: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 368-373.
- Cooper, J. R., Reneau, Jr., R. B., Kroontje, W., and Jones, G. D., 1984, Distribution of nitrogenous compounds in a rhodic paleudult following heavy manure application: *Jour. Environ. Qual.*, v. 13, p. 189-193.
- Dao, T. H., Lavy, T. L., and Sorensen, R. C., 1979, Atrazine degradation and residue distribution in soil: *Soil Sci. Soc. Am. Jour.*, v. 43, p. 1129-1134.
- Doran, J. W., Wilhelm, W. W., and Power, J. F., 1984, Crop residue removal and soil productivity with no-till corn, sorghum, and soybean: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 640-645.
- Dorsch, M. M., Scragg, R. K., McMichael, A. J., Baghurst, P. A., and Dyer, K. F., 1984, Congenital malformations and maternal drinking water supply in rural South Australia: a case control study: *Am. Jour. Epidemiol.*, v. 119, p. 473-486.
- Duff, J. H., Triska, F. J., and Oremland, R. S., 1984, Denitrification associated with stream periphyton: chamber estimates from undisrupted communities: *Jour. Environ. Qual.*, v. 13, p. 514-518.
- Duxbury, J. M., Bouldin, D., Terry, R. E., and Tate, R. L. III, 1982, Emissions of nitrous oxide from soils: *Nature*, v. 298, p. 462-464.
- El-Haris, M. K., Cochran, V. L., Elliott, L. F., and Bezdicek, D. F., 1983, Effect of tillage, cropping, and fertilizer management on soil nitrogen mineralization potential: *Soil Sci. Soc. Am. Jour.*, v. 47, p. 1157-1161.
- Ellis, J. R., Mielke, L. N., and Schuman, G. E., 1975, The nitrogen status beneath beef cattle feedlots in eastern Nebraska: *Soil Sci. Soc. Am. Proc.*, v. 39, p. 107-111.
- Erbach, D. C., 1982, Tillage for continuous corn and corn-soybean rotation: *Trans. Am. Soc. Agric. Eng.*, v. 25, p. 906-922.
- Feigenbaum, Sala, Seligman, N. G., and Benjamin, R. W., 1984, Fate of nitrogen-15 applied to spring wheat for three consecutive years in a semi-arid region: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 838-843.
- Fox, R. H., and Piekielek, W. P., 1984, Relationships among anaerobically mineralized nitrogen, chemical indexes, and nitrogen availability to corn: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 1087-1090.

- Frank, R., Braun, H. E., Van Hove Holdrinet, M., Sirons, G. J., and Ripley, B. D., 1982, Agriculture and water quality in the Canadian Great Lakes Basin: V. pesticide use in 11 agricultural watersheds and presence in stream water, 1975-1977: *Jour. Environ. Qual.*, V. 11, p. 497-505.
- Fraser, P., and Chilvers, D., 1980, Health aspects of nitrate in drinking water: *The Science of the Environ.*, Water Supply and Health, *Studies in Environ. Sci.*, v. 12, p. 103-116.
- Frere, M. H., Ross, J. D., and Lane, J. L., 1980, The nutrient submodel; In Knisel, W. G., ed.: *Creams: A Field Scale Model for Chemical, Runoff, and Erosion from Agricultural Management Systems*, v. III, rept. 26., U.S.D.A., Washington, D.C.
- Gambrell, R. P., Gilliam, J. W., and Weed, S. B., 1975a, Denitrification in subsoils of the North Carolina coastal plain as affected by soil drainage: *Jour. Environ. Qual.*, v. 4, p. 311-316.
- Gambrell, R. P., Gilliam, J. W., and Weed, S. B., 1975b, Nitrogen losses from soils of the North Carolina coastal plain: *Jour. Environ. Qual.*, v. 4, p. 317-323.
- Gast, R. G., Nelson, W. W., and Randall, G. W., 1978, Nitrate accumulation in soils and loss in tile drainage following nitrogen application to continuous corn: *Jour. Environ. Qual.*, v. 7, p. 258-262.
- Germann, P. F., Edwards, W. M., and Owens, L. B., 1984, Profiles of bromide and increased soil moisture after infiltration into soils with macropores: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 237-244.
- Ghadiri, H., Shea, P. J., Wicks, G. A., and Haderlie, L. C., 1984, Atrazine dissipation in conventional-till and no-till sorghum: *Jour. Environ. Qual.*, v. 13, p. 549-552.
- Glotfelty, D. E., Taylor, A. W., Isensee, A. R., Jersey, J., and Glenn, S., 1984, Atrazine and simazine movement to Wye River Estuary: *Jour. Environ. Qual.*, V. 13, p. 115-121.
- Goodroad, L. L., Keeney, D. R., and Peterson, L. A., 1984, Nitrous oxide emissions from agricultural soils in Wisconsin: *Jour. Environ. Qual.*, v. 13, p. 557-561.
- Goring, C. A. I., and Laskowski, D. A., 1982, The effects of pesticides on nitrogen transformations in soils; In, Stevenson, ed.: *Agronomy Monograph* no. 22, ASA-CSSA-SSSA, Madison, Wisc., p. 689-720.
- Hall, J. K., 1974, Erosional losses of s-triazine herbicides: *Jour. Environ. Qual.*, v. 3, p. 174-180.
- Hall, J. K., Hartwig, N. L., and Hoffman, L. D., 1983, Application mode and alternate cropping effects on atrazine losses from a hillside: *Jour. Environ. Qual.*, v. 12, p. 336-340.

- Hall, J. K., Hartwig, N. L., and Hoffman, L. D., 1984, Cyanazine losses in runoff from no-tillage corn in "living" and dead mulches vs. unmulched, conventional tillage: *Jour. Environ. Qual.*, v. 13, p. 105-110.
- Hall, J. K., Pawlus, M., and Higgins, E. R., 1972, Losses of atrazine in runoff water and soil sediment: *Jour. Environ. Qual.*, vo. 1, p. 172-176.
- Hallberg, G. R., 1980, Pleistocene stratigraphy in east-central Iowa: *Ia. Geol. Surv. Tech. Info. Ser. no. 10*, 168 p.
- Hallberg, G. R., and Hoyer, B. E., 1982, Sinkholes, hydrogeology, and groundwater quality in northeast Iowa: *Ia. Geol. Surv., Open-File Rept. 82-3*, 120 p.
- Hallberg, G. R., Hoyer, B. E., Bettis, E. A., III, and Libra, R. D., 1983, Hydrogeology, water quality, and land management in the Big Spring basin, Clayton County, Iowa: *Ia. Geol. Surv., Open-File Rept. 83-3*, 191 p.
- Hallberg, G. R., Libra, R. D., Ressmeyer, G. G., Bettis, E. A., III, and Hoyer, B. E., 1984, Temporal changes in nitrates in groundwater in northeastern Iowa: *Iowa Geol. Surv., Open-File Rept. 84-1*, 10 p.
- Hallberg, G. R., Lucas, J. R., and Goodmen, Catherine M., 1978, Part I. Semi-quantitative analysis of clay mineralogy, *in* Standard procedures for evaluation of Quaternary materials in Iowa, *Ia. Geol. Survey, Tech. Info. Ser.*, no. 8, p. 5-21.
- Hargett, N. L., and Berry, J. T., 1983, 1982 fertilizer summary data: Natl. Fert. Develop. Ctr., TVA, Muscle Shoals, Alabama, 136 p.
- Harmon, L., and Duncan, E. R., 1978, A technical assessment of nonpoint pollution in Iowa: Contract Report 77-001 to the Iowa Dept. Soil Conserv., College of Agric., Iowa State Univ., 427 p.
- Harris, C. I., Wollson, E. A., and Hummer, B. E., 1969, Dissipation of herbicides at three soil depths: *Weed. Sci.*, v. 17, p. 27-31.
- Hauck, R. D., and Bremner, J. M., 1976, Use of traces for soil and fertilizer nitrogen research: *Adv. Agron.*, v. 28, p. 219-266.
- Heitmann, N., 1980, Water source of Big Spring Trout Hatchery, Clayton County, Iowa: *Proc. Ia. Acad. Sci.*, v. 87, p. 143-147.
- Jacobson, R. L., and Langmuir, D., 1970, The chemical history of some spring waters in carbonate rocks: *Ground Water*, v. 8., No. 32, p. 5-9.
- Johnson, H. P., and Baker, J. L., 1982, Field-to-stream transport of agricultural chemicals and sediment in an Iowa watershed: Part I. Data base for model testing (1976-1978). U.S.D.A., Washington, D.C.
- Jolley, V. D., 1974, Theoretical and measured soil acidity from N-fertilizer as related to the N recovered in crops and soils: Unpub. M.S. thesis, Dept. of Agronomy, Ia. State Univ., Ames, IA, 166 p.

- Jolley, V. D., 1976, Yields of corn and soybeans and the depth of nitrate removal from the soil as influenced by applied and residual nitrogen: Unpub. Ph.D. dissertation, Dept. of Agronomy, Ia. State Univ., Ames, IA., 174 p. (Diss. Abstr., v. 37, 11, B, p. 5476; Univ. Microfilms, Ann Arbor, Mich.).
- Jolley, V. D., and Pierre, W. H., 1977, Profile accumulation of fertilizer-derived nitrate and total nitrogen recovery in two long term nitrogen-rate experiments with corn: *Soil Sci. Soc. Am. Jour.*, v. 41, p. 373-378.
- Jones, T. W., Kemp, W. M., Stevenson, J. C., and Means, J. C., 1982, Degradation of atrazine in estuarine water/sediment systems and soils: *Jour. Environ. Qual.*, v. 11, p. 632-637.
- Junk, G. A., Spalding, R. F., and Richard, J. J., 1980, Areal, vertical, and temporal differences in groundwater chemistry: II. Organic constituents: *Jour. Environ. Qual.*, v. 9, p. 479-483.
- Kanwar, R. S., Johnson, H. P., and Baker, J. L., 1983, Comparison of simulated and measured nitrate losses in tile effluent: *Trans. Am. Soc. Agric. Eng.*, v. 26, p. 1451-1457.
- Keeney, D. R., 1982, Nitrogen management for maximum efficiency and minimum pollution; In, Stevenson, F. J., ed.: *Agronomy Monograph 22*, p. 605-649.
- Khdyer, I. I. and Cho, C. M., 1983, Nitrification and denitrification of nitrogen fertilizers in a soil column: *Soil Sci. Soc. Am. Jour.*, v. 47, p. 1134-1139.
- Kosinski, R. J., and Merkle, M. G., 1984, The effect of four terrestrial herbicides on the productivity of artificial stream algal communities: *Jour. Environ. Qual.*, v. 13, p. 75-82.
- Lafren, J. M., and Colvin, T. S., 1981, Effect of crop residue on soil loss from continuous row cropping: *Trans. Am. Soc. Agric. Eng.*, v. 24, p. 605-609.
- Langmuir, Donald, 1971, The geochemistry of some carbonate groundwaters in central Pennsylvania: *Geochim. Cosmochim. Acta.*, v. 35, p. 1023-1045.
- Libra, Robert D., Hallberg, George R., Ressmeyer, Gale G., and Hoyer, Bernard E., 1984, 1. Groundwater quality and hydrogeology of Devonian-carbonate aquifers in Floyd and Mitchell counties, Iowa: *Ia. Geol. Surv., Open-File Rept.*, 84-2, p. 1-106.
- Linau, Charles W., and Spalding, Roy F., 1984, Major procedural discrepancies in soil extracted nitrate levels and nitrogen isotopic values: *Ground Water*, v. 22, p. 273-278.
- Linn, D. M., and Doran, J. W., 1984, Aerobic and anaerobic microbial populations in no-till and plowed soils: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 794-799.

- Lowrance, R. R., Todd, R. L., and Asmussen, L. E., 1984, Nutrient cycling in an agricultural watershed: 1. Phreatic movement: *Jour. Environ. Qual.*, v. 13, p. 22-27.
- Martin, C. D., Baker, J. L., Erbach, D. C., and Johnson, H. P., 1978, Washoff of herbicides applied to corn residue: *Trans Am. Soc. Agric. Eng.*, v. 21, p. 1,164-1,168.
- Massey, H. F., and Jackson, M. L., 1952, Selective erosion of soil fertility constituents: *Soil Sci. Soc. Am. Proc.*, v. 16, p. 353-356.
- McDowell, L. L., and McGregor, K. C., 1980, Nitrogen and phosphorus losses in runoff from no-till soybeans: *Trans, Am. Soc. Agri. Eng.*, v. 23, p. 643-648.
- McKeague, J. A., Wang, C., and Topp, G. C., 1982, Estimating saturated hydraulic conductivity from soil morphology: *Soil Sci. Soc. Am. Jour.*, v. 46, p. 1239-1244.
- McKenney, D. J., Shuttleworth, K. F., and Findlay, W. I., 1980, Nitrous oxide evolution rates from fertilized soils: effects of applied nitrogen: *Can. Jour. Soil Sci.*, v. 60, p. 429-438.
- Megahan, W. F., and Clayton, J. L., 1983, Tracing subsurface flow on roadcuts on steep, forested slopes: *Soil Sci. Soc. Am. Jour.*, v. 47, p. 1063-1067.
- Mielke, L. N., and Ellis, J. R., 1976, Nitrogen in soil cores and groundwater under abandoned cattle feedlots: *Jour. Environ. Qual.*, v. 5, p. 71-75.
- Moldenhauer, W. C., Langdale, G. W., Frye, W., McCool, D. E., Papendick, R. I., Smika, D. E., and Fryrear, W., 1983, Conservation tillage for erosion control: *Jour. Soil and Water Conserv.*, v. 38, p. 144-151.
- Mosier, A. R., and Hutchinson, G. L., 1981, Nitrous oxide emissions from cropped fields: *Jour. Environ. Qual.*, v. 10, p. 169-173.
- Mueller, D. H., Wendt, R. C., and Daniel, J. C., 1984, Soil and water losses as affected by tillage and manure application: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 896-900.
- Mulvaney, R. L., and Kurtz, L. T., 1984, Evolution of dinitrogen and nitrous oxide from nitrogen-15 fertilized soils cores subjected to wetting and drying cycles: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 596-602.
- Muir, D. C., and Baker, B. E., 1976, Detection of triazine herbicides and their degradation products in tile-drain waters from fields under intensive corn (maize) production: *Jour. Agric. Food and Chem.*, v. 24, p. 122-125.
- National Research Council, 1978, Nitrates: An environmental assessment. Environmental Studies Board, Commission on Natural Resources, Coordinating Committee for Scientific and Technical Assessment of Environmental Pollutants. National Academy of Sciences, Washington, D.C.

- Nelson, W. W., and MacGregor, J. M., 1973, Twelve years of continuous corn fertilization with ammonium nitrate or urea nitrogen: *Soil Sci. Soc. Amer. Proc.*, v. 37, p. 583-586.
- Nelson, W. W., and Randall, G. W., 1983, Fate of residual nitrate-N in a tile-drained mollisol: *Agron. Abstracts*, Am. Soc. Agron., Wash. D.C., p. 215.
- Oliver, J. C., Fairbank, W. C., Meyer, J. L., and Rible, J. M., 1974, Subfloor monitoring of shady grove dairy liquid manure holding pond: *Calif. Agric.*, v. 28, p. 6-7.
- Olsen, R. J., Hensler, R. F., Attoe, O. J., Witzel, S. A., and Peterson, L. A., 1970, Fertilizer nitrogen and crop rotation in relation to movement of nitrate nitrogen through soil profiles: *Soil Sci. Soc. Amer. Proc.*, v. 34 p. 448-452.
- Olsen, R. J., Hensler, R. F., Attoe, O. J., Witzel, S. A., and Peterson, L. A., 1970, Fertilizer nitrogen and crop rotation in relation to movement of nitrate nitrogen through soil profiles: *Soil Sci. Soc. Am. Proc.*, v. 34, p. 448-452.
- Olson, R. V., and Swallow, C. W., 1984, Fate of labeled nitrogen fertilizer applied to winter wheat for five years: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 583-586.
- Onstad, C. A., and Otterby, M. A., 1979, Crop residue effects on runoff: *Jour. Soil and Water Conserv.*, v. 34, p. 94-96.
- Owens, L. D., 1960, Nitrogen movement and transformation in soils as evaluated by a lysimeter study utilizing isotopic nitrogen: *Soil Sci. Soc. Amer. Proc.*, v. 24, p. 372-376.
- Owens, L. B., Edwards, W. M., and Van Keuren, R. W., 1983a, Surface runoff water quality comparisons between unimproved pasture and woodland: *Jour. Environ. Qual.*, v. 12, p. 518-522.
- Owens, L. B., Van Keuren, R. W., and Edwards, W. M., 1983b, Nitrogen loss from a high-fertility, rotational pasture program: *Jour. Environ. Qual.*, v. 12, p. 346-350.
- Owens, L. B., Edwards, W. M., and Van Keuren, R. W., 1984, Peak nitrate-nitrogen values in surface runoff from fertilized pastures: *Jour. Environ. Qual.*, v. 13, p. 310-312.
- Pan, W. L., Kamprath, E. J., Moll, R. H., and Jackson, W. A., 1984, Prolificacy in corn: its effects on nitrate and ammonium uptake and utilization: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 1101-1106.
- Pierre, D., 1983, The impact of agriculture on water quality: *Fertilizers and Agric.*, no. 85, p. 51-62.

- Pettyjohn, W. A., 1982, Cause and effect of cyclic changes in ground water in Hall County, Nebraska: *Ground Water*, v. 11, no. 6, p. 4-13.
- Quisenberry, V. L., and Phillips, R. E., 1976, Percolation of surface applied water in the field: *Soil Sci. Soc. Am. Jour.*, v. 40, p. 484-489.
- Quisenberry, V. L., and Phillips, R. E., 1978, Displacement of soil water by simulated rainfall: *Soil Sci. Soc. Am. Jour.*, v. 42, p. 675-679.
- Rauschkolb, R. S., Brown, A. L., Salisbury R. L., Quick, J., Prato, J. D., Pelton, R. E., and Kegel, F. R., 1974, Rapid tissue testing for evaluating nitrogen nutritional status of (1) corn and (2) sorghum: *Calif. Agric.*, v. 28, p. 10-13.
- Rice, C. W., and Smith, M. Scott, 1982, Denitrification in no-Till and plowed soils: *Soil Sci. Soc. Am. Jour.*, v. 46, p. 1168-1173.
- Rice, C. W., and Smith, M. S., 1983, Nitrification of fertilizer and mineralized ammonium in no-till and plowed soil: *Soil Sci. Soc. Am. Jour.*, v. 47, p. 1125-1129.
- Rice, C. W., and Smith, M. S., 1984, Short-term immobilization of fertilizer nitrogen at the surface of no-till and plowed soils: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 295-297.
- Ritter, W. F., Johnson, H. P., Lovely, W. G., and Molnau, M., 1974, Atrazine, propachlor, and diazinon residues on small agricultural watersheds, runoff losses, persistence, and movement: *Environ. Sci. Technol.*, v. 8, p. 38-42.
- Ritter, W. F., Walpole, E. W., and Eastburn, R. P., 1980, An anaerobic lagoon for swine manure and its effect on the groundwater quality in sandy-loam soils; In *Livestock Waste: A Renewable Resource, Proc. of 4th Inter. Symp. Livestock Wastes*, p. 244-246.
- Robbins, C. W., and Carter, D. L., 1980, Nitrate-nitrogen leached below the root zone during and following alfalfa: *Jour. Environ. Qual.*, v. 9, no. 3, p. 447-450.
- Roeth, F. W., Lavy, T. L., and Burnside, O. C., 1969, Atrazine degradation in two soil profiles: *Weed Sci.*, v. 17, p. 202-205.
- Rolston, D. E., Sharpley, A. N., Toy, D. W., and Broadbent, F. E., 1981, Field measurement of denitrification: III. Rates during irrigation cycles: *Soil Sci. Soc. Am. Jour.*, v. 46, p. 289-296.
- Romkens, M. J. M., and Nelson, D. W., 1974, Phosphorus relationships in runoff from fertilized plots: *Jour. Environ. Qual.*, v. 3, p. 10-13.
- Romkens, M. J. M., Nelson, D. W., and Mannering, J. V., 1973, Nitrogen and phosphorus composition of surface runoff as affected by tillage method: *Jour. Environ. Qual.*, v. 2, p. 292-295.

- Schaller, F. W., and Bailey, G. W., eds., 1983, *Agricultural Management and Water Quality*: Ia. State Univ. Press, Ames, Ia., 472 p.
- Schwab, G. O., McLean, E. O., Waldron, A. C., White, R. K., and Michener, D. W., 1973, Quality of drainage water from a heavy-textured soil: *Trans. Am. Soc. Agric. Eng.*, v. 16, no. 6, p. 1104-1107.
- Seiler, W., and Conrad, R., 1981, Field measurements of natural and fertilizer-induced N₂O release rates from soils: *Jour. Air Pollut. Control Fed.*, v. 31, p. 767-772.
- Shufford, J. W., Fritto, D. D., and Baker, D. E., 1977, Nitrate-nitrogen and chloride movement through undisturbed field soil: *Jour. Environ. Qual.*, v. 6, p. 255-259.
- Simpson, T. W., and Cunningham, R. L., 1982, The occurrence of flow channels in soils: *Jour. Environ. Qual.*, v. 11, p. 29-30.
- Singh, K. P., and Stall, J. B., 1971, Derivation of base flow recession curves and parameters: *Water Resources Res.*, v. 7, no. 2, p. 292-303.
- Smart, P. L., and Laidlow, I. M. S., 1977, An evaluation of some fluorescent dyes for water tracing: *Water Resources Res.*, v. 13, p. 15-33.
- Smith, C. J., and DeLaune, R. D., 1983, Nitrogen loss from fresh-water and saline estuarine sediments: *Jour. Environ. Qual.*, v. 12, p. 514-518.
- Spalding, R. F., Junk, G. A., and Richard, J. J., 1980, Pesticides in groundwater beneath irrigated farmland in Nebraska, August 1978: *Pesticides Monitoring Jour.*, v. 14, no. 2, p. 70-73.
- Stevenson, F. J., ed., 1982, Nitrogen in Agricultural Soils: *Agronomy Monograph 22*, 940 p.; ASA-CSSA-SSSA, Inc., Madison, Wisc.
- Stoltenberg, N. L., and White, J. L., 1953, Selective losses of plant nutrients by erosion: *Soil Sci. Soc. Am. Proc.*, v. 17, p. 406-410.
- Swank, W. T., and Caskey, W. H., 1982, Nitrate depletion in a second-order mountain stream: *Jour. Environ. Qual.*, v. 11, p. 581-584.
- Thomas, G. W., and Phillips, R. E., 1979, Consequences of water movement in macropores: *Jour. Environ. Qual.*, v. 8, p. 149-152.
- Timmons, D. R., 1984, Nitrate leaching as influenced by water application level and nitrification inhibitors: *Jour. Environ. Qual.*, v. 13, p. 305-309.
- Timmons, D. R., and Dylla, A. S., 1981, Nitrogen leaching as influenced by nitrogen management and supplemental irrigation level: *Jour. Environ. Qual.*, v. 10, p. 421-426.
- Triplett, G. B., Conner, B. J., and Edwards, W. M., 1978, Transport of atrazine and simazine in runoff from conventional and no-tillage corn: *Jour. Environ. Qual.*, v. 7, p. 77-84.

- Tyler, D. D., and Thomas, G. W., 1977, Lysimeter measurements of nitrate and chloride losses from soil under conventional and no-tillage corn; *Jour. Environ. Qual.*, v. 6, p. 63-66.
- Van Doren, D. M., Jr., Moldenhauer, W. C., and Triplett, G. B. Jr., 1984, Influence of long-term tillage and crop rotation on water erosion: *Soil Sci. Soc. Am. Jour.*, v. 48, p. 636-640.
- Von Stryk, F. G., and Botton, E. F., 1977, Atrazine residue in tile drain water from corn plots as affected by cropping practices and fertility level: *Can. Jour. Soil Sci.*, v. 57, p. 249-253.
- Wauchope, R. D., 1978, The pesticide content of surface water draining from agricultural fields -- a review: *Jour. Environ. Qual.*, v. 7, p. 459-472.
- Wehtje, L., Mielke, L. N., Leavitt, J. R. C., and Schepers, J. S., 1984, Leaching of atrazine in the root zone of an alluvial soil in Nebraska: *Jour. Environ. Qual.*, p. 13, p. 507-513.
- Wehtje, G. R., Spalding, R. F., Burnside, O. C., Lowry, S. R., and Leavitt, J. R. C., 1983, Biological significance and fate of atrazine under aquifer conditions: *Weed. Sci.*, v. 31, p. 610-618.
- Westerman, R. L., and Kurtz, L. T., 1973, Priming effect of ¹⁵N labeled fertilizers on soil nitrogen in field experiments: *Soil Sci. Soc. Am. Proc.*, v. 37, p. 725-727.
- Wu, T. L., Correll, D. L., and Remenapp, H. E. H., 1983, Herbicide runoff from experimental watersheds: *Jour. Environ. Qual.*, v. 12, p. 330-336.

APPENDIX 1

Standard Water-Quality Data From All Monitoring Sites

Locations given on figures 3, 4, and 5, and in Hallberg et al., 1983.

Notes: Pesticide analyses are given in $\mu\text{g/l}$ with a single-letter abbreviation for the particular pesticide. The abbreviations are as follows: A - Atrazine or AAtrex (atrazine); B - Bladex (cyanazine); D- Dual (metolachlor); F - Dyfonate (fonofos); L - Lasso (alachlor); R - Furadan (carbofuran); S - Sencor/Lexone (metribuzin); and N - dieldrin; ND - none detected; N/A or blank - not analyzed.

N-series, or nitrogen-series analyses are reported in mg/l as N, for T - $\text{NO}_3 + \text{NO}_2\text{-N}$; G - organic-N; A - ammonium-N; and $\text{NO}_2\text{-N}$ for $\text{NO}_2\text{-N}$ when it was analyzed separately (when $\text{NO}_2\text{-N}$ appears, T is only $\text{NO}_3\text{-N}$).

Other: abbreviations; M-complete mineral scan, data in Appendix 2; 0 - other see table for miscellaneous data for that site.

Some surfacewater sites will report water discharge measurements, Q = cfs; and suspended sediment concentrations (sus. sed. con. = mg/l).

Table 1-1. Water analyses for well VD-24 (site 11).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
11/17	17	0								
<u>1982</u>										
1/26	10	0								
2/25	28	2.2	600+59	7.3	0.64					
3/23	26	2.2	--	7.3	0.41					
4/19	20	0	350+34	7.4	1.1					
5/26	19	0	510+50	7.4	1.5	11.0	700			
6/8								0.06A		
6/22	18	0	450+48	7.4	0.57	11.0	740			
7/28	57	0	810+80	7.2	0.48	11.0	705	N.D.	M	
8/24	24	0	400+45	6.9	1.6	13.5	720			
9/22	38	0	380+45	7.5	1.5	10.0	760			
10/26	36	0	490+59	-----		12.0	760			
11/30	31	0	290+35	7.4	1.45	10.0	670			
12/28	24	0	310+37	7.3	0.69	7.5	700			
N	13			10	10		8			
X̄	27			7.3	0.99		720			
S	12				0.48		32			

Table 1-1. Continued.

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or 0
<u>1983</u>									
5/5	21		7.2	11.9	640	4.60T 0.09G 0.02A		14	M
6/28	21	0				4.70T <0.01G <0.01A			
7/6	23					5.20T <0.01G <0.01A	N.D.		
7/28	14	0							
10/3	15			16	715		N.D.		
<u>1984</u>									
5/1	16						N.D.		
6/14	13						N.D.		
7/18	13								
8/28	9								

¹ A - atrazine
N.D. - none detected
µg/l - part per billion

Table 1-2. Water analyses for well B-18 (site 15).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
11/17	144	0								W-17703
<u>1982</u>										
1/26	137	0								
2/24	134	5.1	--	7.2	0.90			N.D.		
3/23	134	5.1	--	7.2	0.55					
4/19	140	2.2	--	7.3	1.1					
5/26	148	5.1	990+91	7.3	3.6					
6/7										
6/22	154	2.2	1300+120	7.4	0.56	11.0	1110	0.06A		
7/28	158	0	1100+103	7.3	0.58	10.5	1200	0.10A		
8/25	141	9.2	900+88	7.1	8.7	10.0	1090	N.D.	M	
9/22	132	0	1700+160	7.4	0.78	9.0	1050			
10/26	144	0	660+74	--	--	10.0	1090			
11/30	142	5.1	790+78	7.5	1.10	9.0	1100			
12/28	153	9.2	-----	7.1	0.85	9.0	1100			
N	13			7.0	10		10			
X̄	143			7.3	1.9		1100			
S	8			---	2.6		46			

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or 0
<u>1983</u>									
5/5	142			12	1150				
6/28	144	0				32.00T 0.04G 0.01A			
7/6	140					31.00T <0.01G <0.01A	N.D.		
7/28	154	2.2							
10/3	158			14	1115				

Table 1-3. Water analyses for well B-32 (site 16).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
11/18	19	0								
<u>1982</u>										
1/26	19	5.1								
2/24	17	0	--	7.5	39					
3/23	16	0	--	7.4	22					
4/19	15	0	--	7.6	6.3					
5/26	12	0	150+17	7.6	20	9.0	605			
6/7										
6/22	18	0	440+48	7.6	10.5	9.4	700	N.D.		
7/28	19	0	300+30	7.4	0.35	10.0	700	N.D.	M	
8/25	14	0	140+21	7.3	54	9.0	680			
9/22	18	0	140+20	7.6	2.75	9.0	685			
10/26	17	0	91+26			10.0	680			
11/30		out of order								
12/28	21	0	-----	7.4	21	7.0	675			
N	12			9	9		7			
X̄	17			7.5	20		675			
S	3				18		32			

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or 0
<u>1983</u>									
5/5	23		7.4	12.5	700	5.10T 0.08G 0.06A			9.0 M (sample turbid)
10/3	24			13.5	690				

Table 1-4. Water analyses for well VD-12 (site 26).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
11/16	12	0								
<u>1982</u>										
1/26	26	16+								sampled at cistern
2/15	<5	0	320+34	7.4	>100					
3/23	<5	0	490±50	7.3	58					
4/19	--	--	--	--	--	--	--			
5/26	<5	0	870+84	7.4	78	10.5	810			
6/7								0.06A		
6/22	<5	0	260+27	7.4	63.5	9.7	840			
7/28	36	2.2	820±75	7.2	3.55	10.0	830	N.D.	M	
8/25	<5	0	390±44	7.1	42	9.5	800			
9/22	<5	0	480±53	7.4	21	9.5	780			
10/26	63	0	590±68	-----	-----	9.0	790			
11/30	10	0	730±74	7.2	34.5	9.0	675			
12/28	34	16+	-----	7.2	5.1	9.0	890			
N	12			9	9		8			
X	16			7.3	45		800			
S	20			---	33		62			

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or O
<u>1983</u>									
5/5	6.4		7.3	11.9	840	1.40T 0.11G 0.14A		9.0	M (sample turbid)
7/6	28								
10/3	<5			14	775				

Table 1-5. Water analyses for well B-27 (site 30).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
11/18	40	9.2								
<u>1982</u>										
1/26	43	0								
2/24	72	9.2	--	7.3	27					
3/23	38	0	--	7.3	0.91					
4/19	31	0	--	7.6	14					
5/26	35	0	1100+100	7.5	14	9.0	700			
6/7								0.05A		
6/22	38	0	940+91	7.4	15	9.7	720			
7/28	41	16+	1200±110	7.4	1.2	10.0	700	N.D.	M	
8/25	24	5.1	560±60	7.1	14	9.5	700			
9/22	23	5.1	760±81	7.4	7.4	8.5	710			
10/26	30	0	630±72	-----	-----	9.5	710			
11/30	27	9.2	750±74	7.4	78	9.0	690			
12/28	28	5.1	-----	7.3	9.5	7.0	675			
N	13			10	10		8			
X	36			7.4	18		700			
S	13			---	22		14			

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or O
<u>1983</u>									
5/5	29		7.3	12	700				3.0 M (sample turbid)
10/3	39			14	710				

Table 1-6. Water analyses for well VD-18 (site 37).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
11/17	94	2.2								
<u>1982</u>										
1/26	88	2.2								
2/25	94	0	1000+95	7.2	31			N.D.		
3/23	36	16+	1200±110	7.2	2.6					
4/19	84	16	800±82	7.3	3.4					
5/26	27	0	850±81	7.3	8.9	10.0	745			
6/7								0.12A		
6/22	62	2.2	1100+100	7.4	7.8	10.2	900	0.10A		
7/28	152	2.2	810±77	7.2	3.3	10.0	950	0.09A	M	
8/24	114	0	930±94	7.0	3.0	10.0	980			
9/22	106	2.2	1100±110	7.3	5.2	10.0	960			
10/26	81	0	840±89	-----		9.0	1000			
11/30	77	2.2	770±77	7.2	25	10.0	900			
12/28	74	0	-----	7.3	33	9.0	930			
N	13			10	10		8			
X̄	84			7.2	12		920			
S	32			---	12		79			

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or 0
<u>1983</u>									
5/5	62		7.3	12.5	900			34	
10/3	103			15	940				

Table 1-7. Water analyses for well L-7 (site 39).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
11/16	120	16+								
<u>1982</u>										
1/26	142	0								
2/24	71	0	--	7.4	0.76					
3/23	108	16+	--	7.4	3.7					
4/19	109	0	--	7.3	1.8					
5/26	109	0	750±73	7.3	1.4	10.0	1075			
6/7										
6/22	--	--	--	--	--	11.6	610	0.05A		
7/28	59	2.2	420+40	7.3	0.53	12.0	1200	N.D.	M	
8/25	123	0	230±33	6.4	10	11.0	1275			
9/22	84	5.1	280±36	7.5	0.89	10.0	1150			
10/26	120	5.1	350±46	-----		10.5	1330			
11/30	108	16+	550±58	7.5	0.98	9.0	1100			
12/28	45	0	-----	7.4	0.95	8.5	535			
N	12			9	9		8			
X̄	100			7.1	2		1030			
S	29			---	3		300			

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or 0
<u>1983</u>									
5/5	140		7.2	12	1200		0.11A	80	M
10/3	156			13.5	1140				

Table 1-8. Water analyses for well PAT-20 (site 45).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
11/18	<5	0								
<u>1982</u>										
1/26	<5	0								
2/25	<5	0	250+28	7.1	5.5					
3/23	<5	0	--	7.2	>100					
4/19	<5	0	210+23	7.2	22					
5/26	<5	0	260+30	7.3	4.5	11.5	650			
6/7								N.D.		
6/22	<5	0	290+35	7.3	26	11.4	680			
7/28	<5	0	170+24	7.3	2.0	11.0	680	N.D.	M	
8/24	<5	0	240+34	6.9	12	11.5	655			
9/22	<5	0	210+31	7.8	2.7	10.0	680			
10/27	<5	0	200+30	-----	-----	11.0	700			
11/30	<5	0	180+20	7.2	5.9	10.0	665			
12/28	<5	0	-----	7.2	3.0	9.0	655			
N	13			10	10		8			
X	<5			7.2	18		670			
S	0			---	30		17			

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or 0
<u>1983</u>									
5/5	0.7		7.3	14	680	0.20T 0.06G 0.22A		<0.5	M
10/3	<5			14	665				

Table 1-9. Water analyses for well PAT-18 (site 47).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
11/18	<5	0								
<u>1982</u>										
1/26	<5	0	83+12							
2/25	<5	2.2	110+15	7.3	11					N.D.
3/23	<5	0	130+17	7.3	37					
4/19	<5	0	120+15	7.4	57					
5/26	<5	0	110+17	7.4	9.5	9.5	585			
6/7										N.D.
6/22	<5	0	170+24	7.5	34	10.4	600			N.D.
7/28	<5	0	180+23	7.4	10	11.0	590			N.D.
8/24	<5	0	150+24	7.3	61	11.0	600			M
9/22	<5	0	110+17	7.5	5.5	10.0	600			
10/27	<5	0	130+20	-----	-----	10.0	620			
11/30	<5	0	110+15	7.4	32	9.0	605			N.D.
12/28	<5	0	52+12	7.3	55	8.0	610			
N	13			10	10		8			
X	<5			7.4	31		600			
S	0			---	22		11			

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or 0
<u>1983</u>									
3/4/83	<5								
5/5	<0.1		7.4	11	600	<0.01T 0.07G 0.11A	N.D. N.D.	<0.5	M
6/28	<5	0							
6/28	<0.1					<0.01T <0.01G <0.01A			
7/6	<5	0							
7/6	<0.1					<0.01T <0.01G <0.01A	N.D.		
7/28	<5	5.1							
10/3	<5			14	610				

Table 1-10. Water analyses for well F-51 (site 49).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
12/15	11	0								
<u>1982</u>										
1/26	12	0								
2/25	26	0	1300+120	7.3	3.1					
3/23	17	0	1800±160	--	--					
4/19	42	2.2	1700±150	7.2	2.5					
5/26	25	5.1	--	7.2	10	10.0	695			
6/7								0.45A		
6/22	39	9.2	790+74	7.5	4.9	10.5	810			
7/28	35	0	1100±110	7.4	0.78	11.0	705	N.D.	M	
8/24	11	0	2100±190	7.2	3.2	11.0	650			
9/22	10	0	1800±180	7.8	0.90	10.0	630			
10/26	10	0	1700±160	-----	-----	10.0	665			
11/30	52	5.1	790±78	7.2	32	10.0	825	0.16A		
12/28	30	2.2	-----	7.1	2.1	8.0	600			
N	13			9	9		8			
X	25			7.3	7		690			
S	14			---	10		81			

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or 0
<u>1983</u>									
5/5	11		7.4	12.2	640			14	M
10/3	24			15	740				

Table 1-11. Water analyses for well F-8 (site 52).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
12/14	64	0								
<u>1982</u>										
1/26	59	0								
2/25	62	0	1200+110	7.3	0.56					
3/23	63	0	1300±130	7.3	0.42					
4/19	79	0	1000±96	7.0	3.4					
5/26	63	0	1500±130	7.6	0.90	10.5	735			
6/7										
6/22	63	0	1600+150	7.5	0.50	11.2	775	0.25A		
7/28	61	0	1400±130	7.5	0.56	10.5	745	0.15A	M	
8/25	60	0	1100±124	7.3	1.4	10.0	745			
9/22	57	0	1400±140	7.6	0.79	10.0	740			
10/26	55	0	1200±120	-----	-----	10.0	760			
11/30	60	0	1100±110	8.0	1.3	9.0	725	0.13A		
12/28	60	0	-----	7.5	2.8	8.0	740			
N	13			10	10		8			
X	62			7.4	1.3		750			
S	6			---	1		16			

Table 2-11. Continued

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ ug/l	Cl ⁴ mg/l	Other ³ M or 0
<u>1983</u>									
3/4/83	61	2.2					0.18A		
5/5	54		7.2	12	700	12.00T 0.08G 0.04A	N.D.	11	M
6/27	54	0				12.00T			
6/28	54					<0.01G <0.01A			
7/4	70					13.00T	0.25A		
7/6	59					<0.01G <0.01A			
7/23	56	0							
10/3	59			15	700		0.16A		
<u>1984</u>									
5/1	64						0.29A		
6/14	56						0.20A		
7/18	59								
8/28	58								

¹ A - atrazine
N.D. - none detected
ug/l - part per billion

Table 1-12. Water analyses for well F-33 (site 56).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ ug/l	Other ³ M	Notes
<u>1981</u>										
12/14	35	0								
<u>1982</u>										
1/26	30	0								
2/25	18	16+	980+93	7.3	1					
3/23	34	16+	420+43	7.3	2.5					
4/19	36	2.2	730+69	7.3	1.9					
5/26	48	5.1	920+86	7.3	4.3	--	795			
6/7								0.10A		
6/23	44	0	670+62	7.4	0.53	10.1	800			
7/28	47	2.2	240+28	7.5	0.47	12.0	750	0.15A	M	
8/25	29	0	500+50	7.3	3.7	11.5	710			
9/22	30	0	520+62	7.8	1.7	11.0	710			
10/26	23	0	530+60	-----		10.0	700			
11/30	39	16	790+77	7.3	1.35	9.0	750			
12/29	43	2.2	-----	7.6	2.0	9.0	800			
N	13			10	10		8			
X	35			7.4	1.9		750			
S	9			---	1.3		43			
Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ ug/l	Cl ⁴ mg/l	Other ³ M or 0	
<u>1983</u>										
5/5	38		7.3	10	750					
10/3	32			15	735			11	M	

Table 1-13. Water analyses for well T-17 (site 57).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
11/17	36	2.2								
<u>1982</u>										
1/26	41	2.2								
2/25	38	9.2	1200+110	7.4	0.82					
3/23	44	16+	330+34	7.7	0.82					
4/19	40	2.2	1000+95	7.5	1.1					
5/26	40	16+	900+83	7.5	1.2	--	745	0.20A		
6/7										
6/22	45	16+	980+90	7.5	0.54	10.5	750			
7/28	46	16	780+76	7.5	0.55	12	755	0.14A	M	
8/25	49	16+	330+84	7.4	1.5	9.5	775			
9/22	46	16	1300+130	7.9	0.83	9.0	750			Chlor- inated well 1 week ago
10/26	58	5.1	1200+120	-----		10.0	760			
11/30	58	5.1	1100+110	7.5	0.98	9.0	750			
12/29	52	16+	-----	7.7	1.2	7.0	780			
N	13			10	10		8			
X	46			7.5	0.95		760			
S	7			---	0.30		13			

Table 1-13. Continued

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or O
<u>1983</u>									
5/5	65		7.4	12.7	780	15.00T 0.15G 0.05A		28	M
10/3	77			14	765				
<u>1984</u>									
5/1	81						0.25A		
6/14	66						0.22A		
7/18	93								
8/28	74	0							

¹ A - atrazine
N.D. - none detected
µg/l - part per billion

Table 1-14. Water analyses for well L-42 (site 61).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
11/18	86	0								
<u>1982</u>										
1/26	88	5.1								
2/25	74	5.1	520+51	7.0	4.4			N.D.		
3/23	72	2.2	800+75	7.0	4.0					
4/19	79	0	770+73	7.0	3.4					
5/26	86	16	580+56	7.1	>100.0	--	1260			
6/7								0.04A		
6/23	89	16+	600+42	7.3	19.0	10.1	1290	N.D.		
7/28	104	5.1	570+57	7.1	4.6	11.0	1350	N.D.	M	Well across road from L- 42
8/25	41	16+	340+43	7.2	77.0	10.0	1010			
9/22										dismantled
N	9			7	7		4			
X	80			7.1	30		1220			
S	17			---	41		150			

Table 1-15. Water analyses for well GL-1 (site 72).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
12/14	35	5.1								
<u>1982</u>										
1/26	19	0								
2/25	29	0	460+47	7.2	0.89					
3/23	38	0	930+86	7.2	0.36					
4/19	38	2.2	840+77	7.3	1.3					
5/26	33	0	720+69	7.4	0.87	9.0	690			
6/7								N.D.		
6/22	39	0	750+74	7.4	0.5	11.5	800	N.D.		
7/28	40	5.1	--	7.4	0.46	11.0	855			
8/24	25	16+	400+46	6.9	2.5	14.0	850		M	
9/22	39	16+	500+59	7.3	0.87	13.0	850			
10/27	9	16+	400+47	-----		10.0	940			
11/30	40	2.2	660+66	7.4	0.87	9.0	800			
12/28	36	0	710+73	7.3	0.77	7.0	825			
N	13			10	10		8			
X	32			7.3	0.94		830			
S	10			---	0.61		71			
Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or 0	
<u>1983</u>										
5/5	41		7.2	9	860					
10/3	32			16	905				33	M

Table 1-16. Water analyses for well GL-8 (site 75).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
12/15	90	0								
<u>1982</u>										
1/26	75	16	270+28							
2/25	101	16+	70±11	7.8	10.0			N.D.		
3/23	76	16+	580±57	7.0	0.45					
4/19	88	5.1	460±45	7.2	1.0					
5/27	65	2.2	400±39	7.2	1.4	--	755	N.D.		
6/23	92	16+	210±27	7.4	0.44	13.7	1040	N.D.		
7/28	100	0	--	7.4	0.51	14.0	1010	N.D.	M	
8/25	101	0	220+32	7.6	2.1	14.0	1090			
9/22	83	0	450±53	7.3	1.0	14.0	1000			
10/27	60	5.1	540±61	-----		12.5	925			
11/30	80	16+	530±55	7.1	0.90	10.0	950			
12/29	97	16+	76±14	7.5	1.0	8.0	990			
N	13			10	10		8			
X	85			7.3	1.9		970			
S	14			---	2.9		100			

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or 0
<u>1983</u>									
5/5	94		7.4	14.9	1080			46	M
10/3	95			16.5	1050				

Table 1-17. Water analyses for well AB-6 (site 81).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
1/27	33	2.2								
2/25	32	0	--	7.5	15.0					
3/23	35	16+	--	7.5	2.0					
4/19	33	9.2	--	7.6	2.3					
5/26	34	0	780+74	7.7	2.5	13.0	450			
6/7								0.11A		
6/23	38	0	590+61	7.6	1.4	11.8	500			
7/28	36	0	690±69	7.5	1.45	9.0	560	N.D.	M	
8/24	36	0	550±61	7.2	3.7	12.0	460			
9/22	29	0	720±78	8.1	1.8	11.0	475			
10/27	29	0	690±73	-----		11.0	490			
11/30	35	16+	650±61	7.7	2.9	10.0	490			
12/28	39	16+	400±44	7.5	2.1	8.0	495			
N	12			10	10		8			
X	34			7.5	3.5		490			
S	3			---	4.1		33			

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or 0
<u>1983</u>									
5/5	36		7.5	12.5	480			4.0	M
10/3	39			15	470				

Table 1-18. Water analyses for Big Spring (site 82). Time of sampling between 7:00 and 9:00 A.M. unless noted otherwise.

Date Time	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromohs/cm ² @ 25°C	Pesticide ¹ µg/l	Other M
Water Year - 1982									
10/27/8	47	16+						N.D. (in water or sediment in raceway)	
11/3/81	43	16+							
11/10/81								N.D. (in water or sediment in raceway)	
11/18/81	39	16+							
12/01/81	38	16+							
12/15/81	41	16+						N.D.	
12/22/81	40	16+							
12/29/81	42	16+							
1/12/82	36	16+							
1/19/82	37	16+							
1/26/82			200+22						
2/02/82	35	16+							
2/10/82	35	16+							
2/16/82	33	16+							
2/23/82	30	16+							
2/24/82	30	16+	290+28						
2/25/82	31	16+	230+24 240+24					N.D.	
2/26/82	32	16+	260+26	7.3	9				
3/02/82	35	16+							
3/09/82	26	16+							
3/13/82	23	16+							
3/16/82	23	16+							
3/22/82	35	16+	350+41					N.D. - water (0.65 Dieldrin in sediment from spring)	
3/23/82	38	16+		7.2	13				
4/06/82	39	16+							
4/13/82	40	16+							
4/20/82	41	16+	260+27	7.3	8.7				
4/28/82	42	16+							
5/12/82	40	16+						0.18A	
5/18/82	44	16+						0.44A	
								0.15L	
5/25/82	50	16+							
5/27/82	47	16+							
	7:50 am							0.8A	
								0.2B	
5/27/82	46	16+							
	1:15 pm								
5/27/82	46	16+							
	2:30 pm								
5/27/82	46	16+	240+28						
	9:50 pm								

Table 1-18, con't.

Date Time	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromohs/cm ² @ 25°C	Pesticide ¹ µg/l	Other M
Water Year - 1982 (cont'd.)									
5/28/82	46	16+	350+37	7.4	2.9	9.1	700	2.5A	
	9:00 am							0.15B	
5/28/82	46	16+							
	10:45 am								
5/28/82	45	16+	370+38						
	12:00 pm								
5/30/82	47	16+							
6/01/82	47	16+						0.4A	
								0.7B	
6/07/82			320+36						
6/08/82	45	16+	290+29					0.26A	
6/15/82	47	16+						0.45A	
								0.08B	
								0.08L	
6/23/82	50	16+	310+36	7.4	3.7	9.4	780	0.70A	
								0.09B	
								0.05L	
6/29/82	45	16+						0.75A	
								0.07B	
								0.49A	
								0.49A	
7/06/82									
7/07/82	46	16+							
	8:00 am								
7/07/82	46	16+							
	3:10 pm								
7/08/82	45	16+							
	7:50 am								
7/08/82	45	16+							
	12:50 pm							0.45A	
7/08/82	43	16+							
	3:35 pm								
7/13/82	43	16+						0.31A	
7/21/82	40	16+						0.63A	
7/28/82	36	16+	240+29	7.2	1.75	11.0	670	0.62A	M
8/03/82	41	16+						0.55A	
8/10/82	37	16+							
8/17/82	38	16+							
8/25/82	35	16+							
9/07/82	37	16+						0.26A	
9/14/82	34	16+						0.30A	
9/22/82	35	16+							
								0.28A	
								(8.0 Dieldrin in sediment)	
9/28/82	34	16+							
Water Year - 1983									
10/5/82	33	16+						0.19A	
10/12/82	33	16+						0.20A	

Table 1-18, con't.

Date Time	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromohs/cm ² @ 25°C	Pesticide ¹ µg/l	Other M
Water Year - 1983 (cont'd.)									
10/19/82	34	16+				10.5	750	0.18A	
10/26/82	33	16+	150+23						
End of Water Year - 1982 (See Text for Explanation)									
11/1/82	33	16+						0.10A	
11/3/82								(3.6 Dieldrin and 5.1A in sediment)	
11/9/82									sample bottle broken
11/16/82	57	16+				9.0	740	0.19A	
11/30/82	44	16+	290+29	7.4	4.8			0.11A	
								(1.1 Dieldrin and 5.0A in sediment)	
12/1/82	48	16+						0.22A	
17/7/82	43	16+						0.17A	
12/14/82	50	16+							
12/21/82	51	16+						0.12A	
12/28/82	43	16+	250+30			9.0	705		
10:45 am									
12/28/82			270+32			8.5	610		
12:25 pm									
12/28/82			270+31			9.0	725		
1:20 pm									
12/28/82			230+28			9.0	705		
2:25 pm									
12/28/82			300+34			8.5	680		
3:20 pm									
12/28/82			230+28			8.5	650		
4:20 pm									
12/28/82			290+34			8.5	660		
5:20 pm									
12/28/82			270+32			9.0	700		
7:10 pm									
12/28/82			240+31			9.0	710		
8:10 pm									
12/28/82			280+34			9.0	600		
9:10 pm									
12/28/82			330+37			9.0	705		
10:15 pm									
12/28/82			240+31			9.0	700		
11:10 pm									
12/29/82			320+36			9.0	700		
12:10 am									
12/29/82			240+30			8.0	675		
4:00 am									
12/29/82			240+30			8.0	675		
5:15 am									
12/29/82	45	16+	300+36	7.2	42.5	9.0	655	0.11A	
10:10 am									

Table 1-18 Cont'd.

Date Time	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or O
Calendar Year 1983									
1/04/83	49	All 16+		9	600		0.11A		
1/11/83	48			10	575		0.12A		
1/18/83	51			10	695		0.12A		
1/25/83	46			10	700		0.10A		
2/01/83	46			10	675				
2/08/83	40			10	650		0.11A		
2/15/83	41			10	660				
2/17/83	43								
2/18/83									
7:50am	40								
3:35pm	39								
2/19/83									
8:25am	40								
4:25pm	37								
2/20/83									
1:15am	28								
8:30am	27						0.41A		
12:15pm	25								
5:10pm	23								
11:53pm	17								
2/21/83									
3:20am	19								
8:20am	18						0.67A		
12:50pm	16								
5:00pm	16								
7:15pm	17						0.72A		
9:40pm	18								
2/22/83									
12:05am	17			6	285				
2:10am	15								
4:10am	16								
6:10am	15								
9:15am	14			7.0			0.88A		
							(9.2A in sediment)		
11:45am	14								
1:15pm	14								
2:45pm	14								
3:00pm	16								
5:40pm	17								
2/23/83									
1:12am	22								
7:30am	21			7	370				
10:40am	23			7	360				
6:20pm	22								

Table 1-18 Cont'd.

Date Time	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or O
Calendar Year 1983 (cont'd.)									
2/24/83									
6:45am	27								
12:05pm	27			8	450				
4:00pm	28								
2/25/83									
8:00am	31								
12:00pm	30			8	420				
4:00pm	31								
2/28/83									
8:00am	41								
12:00pm	42			8	640				
4:00pm	41								
3/01/83	40			9	600		0.32A		
3/02/83									
8:00am	32			8	580				
3:35pm	34			9	465				
3/03/83	33			8	540				
3/04/83	36								
3/05/83									
12:30pm	42								
8:00pm	37								
3/06/83	37								
3/08/83	41			9	600		0.16A		
3/09/83	37								
3/10/83	39								
3/11/83	40			10	600				
3/12/83	42								
3/13/83	42								
3/14/83	41								
3/15/83	43			10	580		0.12A		
3/16/83	42			10	580				
3/22/83	44			10	700		0.11A		
3/25/83	43			10	650				
3/26/83	43								
3/27/83	43 (42 Back Spring)								
3/28/83	42			10	710				
3/29/83	44			10	690		0.10A		
4/02/83	43			10	570				
4/03/83	42			9	690				
4/04/83	43			9	650				
4/05/83	51			9	675		0.14A		
4/06/83	51			9	600				
4/07/83	51			9	700				
4/08/83	51			10	645				
4/09/83	50			10	650				
4/10/83	49			9	600				

179

Table 1-18 Cont'd.

Date Time	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or O
Calendar Year 1983 (cont'd.)									
4/11/83	56								
4/12/83	49			10	660		0.16A		
4/13/83	72			10	660				
4/14/83									
8:00am	71			9	550				
3:30pm	69								
4/15/83									
7:45am	73			10	560				
3:45pm	72								
4/16/83	73								
4/17/83	70								
4/18/83	75			10	675				
4/19/83	51			9	700		0.10A		
4/26/83	46			10	700		0.10A		
4/29/83	47			10	700				
4/30/83	48								
5/01/83	49			10	700				
5/04/83	50			10	675		(1.1 Dieldrin in sediment)	16	
5/05/83	50		7.2	11.5	640	10.0T 0.25G 0.02A	0.15A	16	M
5/10/83									
8:00am	44			10	620		0.21A		
2:30pm	42								
5/17/83	45			10	675		0.15A 0.15B 0.08L		
5/18/83	42		7.4	10	720	9.9T 0.05G 0.03A	0.21A	17	M
5/19/83	45		7.3	11	720	10.0T 0.15G 0.07A	0.23A 0.15B 0.24L 0.42A 0.19B 0.32L	16	M
5/22/83	45						0.29A 0.088 0.09L		
5/24/83	47			12	640	10.2T 0.09G 0.15A	0.29A 0.088 0.09L		
5/27/83	54			11	600				
5/31/83	48			12	600		0.24A		
6/03/83	52			11	690				
6/07/83	44			12	750		0.16A		

180

Table 1-18 Cont'd.

*From Mineral Scan

Date Time	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or 0
Calendar Year 1983 (cont'd.)									
6/14/83	46								
6/17/83	46						0.13A		
6/21/83	44								
6/22/83	44			14	700		0.18A		
6/27/83									
8:50am	46			10.8					
3:00pm	48			10.8					
5:00pm	48			10.8			0.23A		
7:45pm	47			10.8					
10:00pm	44*			10.8	720	10.0T 0.18G <0.01A		19.0	M
6/28/83									
12:40am	46			10.8					
6:35am	45			10.7					
11:25am	41*			10.6	710	9.2T 0.18G <0.01A	0.80A 0.19B 0.11L	16	M
1:25pm									
5:30pm	44*			10.6	710	10.0T 0.28G <0.01A	2.5A 0.10B 0.60L 0.41D	19	M
6/29/83									
6:50am	52			10.2					
10:30am	56			10.2					
10:30pm	56			10.2					
6/30/83									
12:30am	50			10.2	730	11.1T 0.33G <0.01A	1.4A 0.29B 0.32L		0
5:00am									
6:45am	48			10.2	700				0
8:00am	47			10.2	740				0
10:40am	44*			10.3	710	10.0T 0.76G 0.01A	1.10A 0.32B 0.28L	18	M,0
3:00pm									
4:00pm	45*			10.3	710	10.0T 0.54G 0.05A	1.90A 0.69B 0.47L	18	M,0
6:00pm									
7:30pm	47			10.3					0
8:30pm	50			10.4	690	11.1T 0.76G 0.01A			0

Table 1-18 Cont'd.

*From Mineral Scan

Date Time	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or 0
Calendar Year 1983 (cont'd.)									
10:20pm	48*			10.5	690	11.1T 0.70G 0.01A	3.1A 1.01B 0.45L	17	0
11:30pm	49			10.5	690				0
7/01/83									
12:30am	48			10.5	690				0
4:30am	48			10.5					0
5:40am	44			10.5	670				0
6:00am	48			10.5	670	10.0T 0.90G 0.01A	1.60A 0.36B 0.38L	14	M,0
9:30am	54			10.5	660	12.0T 1.7G 0.01A	2.10A 0.19B 0.28L		0
10:45am	52			10.5	660				0
11:30am	54			10.5	660		2.30A 0.76B 0.39L		0
1:50pm	53*			10.5	670	12.0T 3.2G 0.7A	2.10 0.62B 0.36L 0.62D	16	M,0
3:00pm									
5:00pm	45			10.5	650				0
5:00pm									
6:00pm	42			10.7	590	10.0T 6.7G 0.16A			0
6:00pm									
8:00pm	42			10.8	560	9.3T 6.5G 0.46A	4.7A 0.43B 0.63L		0
8:00pm									
9:30pm	44			11.0	540	9.3T 5.5G 0.15A			0
10:20pm	44*			11.0	540	10.0T 3.5G 0.17A	3.8A 1.2B 0.62L 0.25D 0.11F	12	M,0
11:30pm									
7/02/83									
12:30am	46			11.0	550				0
1:30am	45			11.0	560	10.0T 3.4G <0.01A	5.1A 0.71B 0.57L		0

*From Mineral Scan

Table 1-18 Cont'd.

Date Time	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ ug/l	Cl ⁴ mg/l	Other ³ M or 0
Calendar Year 1983 (cont'd.)									
7/02/83 (cont'd.)									
5:00am	51			11.0	590				0
6:45am	55			10.9	600				0
9:15am	58			10.9	610				0
11:00am	58			10.9	620		(2.6A and 0.6 Dieldrin on sediment)		0
12:01pm	58			10.8	630				0
3:45pm	57			10.8	640				0
7:30pm	62			10.8	650				0
9:45pm	65			10.8	660		2.0A 0.24B 0.19L		0
7/03/83									
5:00am	65			10.8	685				0
11:59am	64			10.8	700				0
3:00pm	62	(61 Back Spring)		10.7	695				0
6:00pm	63			10.7	700				0
11:45pm	74								0
7/04/83									
7:45am	73			10.6					
7/05/83									
4:30pm	74			10.5	690	13.0T <0.01G <0.01A	0.58A	16	M,0
7/06/83									
7/07/83	72			10.4	730				
7/08/83	72			10.3	730				
7/08/83	55*			10.2	770	12.0T <0.01G <0.01A	0.42A	17	M
7/12/83									
7/19/83	53			(13)	770		0.25A 0.18A		
7/22/83	49								
7/26/83	45						0.17A		
7/29/83	44		7.2		760		0.51A	18	M
8/02/83	46						0.24A		
8/05/83	45								
8/09/83	43						0.27A		
8/16/83	40						0.21A		
8/23/83	43						0.18A		
8/25/83	42								
8/30/83	37						0.35A 0.11L 0.18A 0.19A		
9/06/83	39								
9/13/83	38								
9/16/83	42								
9/20/83	39						0.22A		

Table 1-18 Cont'd.

Date Time	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ ug/l	Cl ⁴ mg/l	Other ³ M or 0
Calendar Year 1983 (cont'd.)									
9/23/83	41								
9/27/83	45						0.24A		
9/30/83	41								
End Water Year 1983									
10/03/83	41			11.5	760				
10/04/83	41					9.4T 0.34G <0.01A	0.19A 0.19A		
10/07/83									
10/11/83	42								
1:30pm	42						0.18A		
5:00pm	42								
9:00pm	41								
11:45pm	40								
10/12/83									
12:30am	40								
8:00am	39						0.20A		
12:30pm	40								
6:00pm	40								
10:30pm	39								
10/13/83									
7:45am	41								
7:00pm	41								
11:30pm	41								
10/14/83	42								
10/16/83	45								
10/18/83	46						0.32A		
10/21/83	47								
10/25/83	51						0.20A		
10/28/83	49								
11/01/83	49						0.24A		
11/03/83	45					10.0T 0.18G 0.02A			
11/04/83									
11/08/83	44								
11/10/83	46						0.18A		
11/10/83	45								
11/15/83	43						0.21A		
11/18/83	44								
11/22/83	45						0.42A		
11/29/83	48						0.22A		
12/02/83	49								
12/06/83	50						0.19A		
12/09/83	47								
12/13/83	47					10.0T 0.03 NO ₂ -N <0.01G <0.01A	0.16A		

Table 1-18 Cont'd.

Date Time	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or O
End Water Year 1983 (cont'd.)									
12/16/83	47								
12/20/83	46								
12/27/83	46								
12/30/83	46								

FOOTNOTES

- Pesticides:
A - Atrazine; B - Bladex; L - Lasso; D - Dual, F - Dyfonate, R - Furadan
 - N-Series:
T - NO₃-N; G - Organic-N; A - Ammonium-N
 - Other:
M - Mineral scan, or other samples, on other tables.
 - Chloride from mineral scan or separate analysis.
- * From Mineral Scan

Table 1-18A. Other water analyses from Big Spring (site 82).

Date Time	Suspended Sediment Concentrations mg/l	Dye-Concentration	
		Fluoresceine µg/l	Amino-G µg/l
5/5/83	17		
6/29/83			
9:00P		0	0
10:30P		0	0
6/30/83			
12:30A	59	10	0
4:30A		40	0
5:20A		50	0
6:45A		270	2
8:00A		35	2
9:40A		180	3
10:40A		150	4
12:01P		30	5
1:00P		90	4
2:00P		60	3
3:00P		90	5
4:00P		110	5
5:00P		100	5
6:00P		90	15
7:30P		100	8
8:30P	72	100	8
9:30P		120	3
10:20P		130	4
11:30P	94	100	3
7/1/83			
12:30A		110	4
5:10A		130	6
7:40A	1660	150	10
8:20A		90	35
9:30A	1870	50	9
10:45A	2220	90	8
11:30A		90	4
12:30P		60	2?
1:50P		40	T
3:00P	2120	50	T
5:00P		0	0
6:00P	4040	0	0
8:00P	3675	40	8
9:30P	1560	10	4
10:20P	1440	0	0
11:30P	1370	20?	6

Table 1-18A. Continued

Date Time	Suspended Sediment Concentrations mg/l	Dye-Concentration	
		Fluoresceine ug/l	Amino-G ug/l
7/2/83			
12:30A	1130	30?	2
1:30A		0	0
5:00A	410	0	0
6:45A		0	0
9:15A		T	0
11:00A	245	0	0
12:00P		0	0
1:30P		0	0
2:30P		0	0
3:45P		0	0
6:00P			
7:30P	65		
9:45P		0	0
7/31/83			
5:00A	60	0	0
9:30A		0	0
12:00P	100	0	0
3:00P		0	0
6:00P	75	0	0
7/5/83	15		
7/8/83	15		
7/27/83	10		
7/28/83	10		
10/12/83	20		

Table 1-19. Water analyses from well AB-3 (site 84).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ ug/l	Other ³ M	Notes
<u>1982</u>										
1/27	14	5.1								
2/25	30	16+	230+27	7.1	11			N.D.		
3/23	35	16+	320+34	7.3	>100					
4/19	38	16+	--	7.3	62					
5/27	60	16+	340+35	7.8	4.0	10.0	955	0.30A 0.20B		
6/23	49	16+	310+36	7.4	23	10.3	910	0.64A 0.11B		
7/28	33	16+	--	7.4	10	11.0	750	0.38A	M	
8/24	5	16+	160+26	7.4	16	10.0	710			
9/22	16	16+	250+36	8.1	>100	10.0	710			
10/26	18	16+	460+54	-----		11.0	750			
11/30	31	16+	630+60	7.5	24.5	10.0	875			
12/29	46	16+	-----	7.9	2.7	9.0	890			
N	12			10	10		8			
X	31			7.4	35		820			
S	16			---	38		99			
Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ ug/l	Cl ⁴ mg/l	Other ³ M or O	Notes
<u>1983</u>										
5/5	37		7.9	12.5	860	8.30T 0.49G 0.01A	0.10A	44	M	
6/28	30					6.60T 0.37G <0.01A				
7/1	26	16+					0.95A			
7/4	51									
7/6	39					8.70T 0.78G 0.02A	0.61A 0.10B			
7/28	21	16+								
10/3	15			13	830		1.10A			

Table 1-20. Water analyses for tile line L-22 T (site 108).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhos/cm ² @ 25°C	Pesticides ¹ ug/l	Other ³ M	Notes
<u>1981</u>										
11/17	97	16+						0.30A		
<u>1982</u>										
1/26	--	--	--	--	--	--	--		--	covered with snow
2/25	32	16+	--	6.9	11.0			N.D.		
3/22	58	16+	--	6.9	5.1					
4/19	81	16+	--	7.0	2.0					
5/26	74	16+	--	7.0	3.2	11.0	575	0.51A		
6/7								1.00A 0.16L		
6/22	86	16+	730+72	7.1	0.61	11.7	675	1.40A		
7/28	86	16+	--	6.8	0.55	--	--			
8/24	70	16+	590+64	6.8	0.81	14.5	590	0.49A		
9/22	65	16+	840+86	7.3	0.78	13	600	0.15A		
10/26	63	16+	830+88	-----		12.0	600	0.30A		
11/30	72	16+	870+85	7.0	0.83	9.0	615			
12/28	79	16+	-----	6.90	1.7	5.0	625	0.30A		
N	12			10	10		7			
X	72			7.0	2.7		610			
S	17			---	3.3		32			

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ ug/l	Cl ⁴ mg/l	Other ³ M or O
<u>1983</u>									
2/22	30	A11 16+					0.49A		
3/3	59								
4/16	70								
5/5	66		7.0	9.8	620	15.00T 0.08G 0.03A	0.24A	20	M

Table 1-20 continued

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ ug/l	Cl ⁴ mg/l	Other ³ M or O
6/17	75	A11					0.39A		
6/28	72	16+				16.00T 0.24G <0.01A			
6/29	91						1.20A		
6/30	107						0.11B		
7/6	91						0.12L		
7/28	67								
8/31	62								
10/3	61			11.5	580		0.35A		
10/11									
10:30A	57								
3:30P	71								
8:30P	73								
10/12									
12:30A	73								
9:00A	71								
1:00P	69								
5:00P	72								
9:30P	69								
10/13									
7:45A	70								
4:30P	70								
10/14									
7:30A	75								
11/3	76								
12/12	63								
12/13	59								
						13.00T 0.28N02 <0.01G <0.01A			

Table 1-22. Water analyses for surface water F-45 (site 110).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
12/15	38	16+								
<u>1982</u>										
1/26	--	--	--	--	--	--	--		--	Frozen
2/25	21	16+	100+15	7.4	26			N.D.		
3/23	35	16+	160±25	7.7	48					
4/19	43	16+	64±12	7.9	25					
5/26	46	16+	60±10	8.0	16	13.0	650			
6/7								17.00A 2.60B 3.00L 6.00D 0.09F		
6/23	54	16+	70±10	8.2	10.3	15.7	710	1.50A 0.41B 0.12L 0.05D		
7/28	32	16+	41+8	8.2	20	22.0	675			
8/25	22	16+	45±10	7.5	14.0	17.0	570			
9/22	27	16+	49±11	7.2	8.3	16.0	695			
10/26	26	16+	60±14	-----	-----	10.0	710			
11/30	40	16+	61±10	8.0	14	4.0	705			
12/28	38	16+	-----	7.6	>100	3.0	420			
N	12			10	10		8			
X	35			7.7	36		640			
S	10			---	32		101			

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or O
<u>1983</u>									
2/22	14	All							
3/3	27	16+							
4/16	68								
5/4	38						0.20A		

Table 1-22. continued

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or O
6/17	42								
6/28	45					10.00T 1.80G 0.43A	8.00A 0.49B 3.00L 2.10D		
6/29	62								
6/30	32								
7/28	38								
8/31	29								
10/3	27			19.7	715				
11/2	68								
12/13	37					8.50T 0.20N02 0.23G 0.07A			

Table 1-23. Water analyses for surface water F-47 (site 111).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1981</u>										
12/15	37	16+								
<u>1982</u>										
1/26	--	--	--	--	--	--	--		--	Frozen
2/25	20	16+	44+12	7.5	24.0			N.D.		
3/23	31	16+	45+10	7.8	65.0					
4/19	44	16+	14+17	8.1	23.0					
5/26	43	16+	25+7	8.1	49.0		635			
6/8								4.50A 1.30B 1.50L 0.70D		
6/23	57	16+	0	8.4	27.0	16.4	720			
7/28	33	16+	-----	8.3	20.0	24.5	650	2.50A 0.39B 0.06L 0.25D	M	
8/25	24	16+	-----	7.4	85.0	17.5	660	2.50A 0.65B 0.31L		
9/21	23	16+	6+.6	8.5	10.1	13.5	655	0.35A		
10/26	21	16+	13+11	-----	-----	9.5	695	0.31A		
11/30	40	16+	51+11	8.1	10.0	5.0	680			
12/29	50	16+	-----	7.8	42.0	-0.5	510	0.30A		
N	12			10	10		8			
X	35			7.9	36		650			
S	12			---	25		63			

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or O
<u>1983</u>									
2/22	14	11					1.00A		
3/3	29	16+							

Table 1-23. continued

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or O
4/16	42								
5/5	40	(Q=28 cfs)	7.3	13	590	9.10T 0.77G 0.04A	0.30A	22	M
6/17	37						0.23A		
6/30	32					7.00T 6.50G 0.72A			
7/6	79						1.50A 0.20B		
7/28	37								
8/31	27								
10/3	25			20	705	6.00T 0.86G 0.01A			
11/2	76					17.00T 0.46G 0.04A			
12/13	36								

Table 1-24. Water analyses for Turkey River (TR-1) (site 113).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromohs/cm ² @ 25°C	Pesticides ¹ ug/l	Other M
<u>1981</u>									
10/27	34	A11 16+							
11/03	28								
11/11	25								
12/04	27								
12/15	33								
12/22	32								
12/29	33								
<u>1982</u>									
1/27	26								
2/23	16								
2/25	20							N.D.	
2/26	22		40+10	7.8	19				
3/02	23								
3/13	12								
3/16	14								
3/22	24								
3/23	26		14+16	7.7	80				
4/06	27								
4/13	27								
4/20	31		10+5	8.8	91				
4/28	29								
5/11	25								
5/18	31								
5/25	43								
5/27	38							3.30A 0.15B 0.40L	
5/28	34		25+5	8.0	49	14.0	545		
6/01	41								
6/08	35							37.00A 5.00B 20.00L 1.60D 0.36F	

Table 1-24, con't.

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromohs/cm ² @ 25°C	Pesticides ¹ ug/l	Other M
6/15	27								
6/23	35		40+11	8.3	24	19.9	600	1.30A 0.10B 0.17L 0.10D	
6/29	29								
7/07									
8:00	25								
3:10	24								
7/08									
7:50	25								
12:55	25								
3:35	25								
7/13	24								
7/21	33								
7/28	36		47+9	7.9	19.5	21.0	545		
8/03	23								
8/10	22								
8/17	19								
8/25	15			7.1	74	17.0	505		
9/7	28								
9/14	24								
9/22	30			7.3	11.0	15.0	585		
9/28	27								
10/05	22								
10/12	25								
10/19	24								
10/26	34		31+3			10.0	575		
11/02	30								
11/09	32								
11/16	37								
11/30	35		26+6	7.4	15	5.0	585		
12/07	27								
12/14	6?								
12/21	36								
12/28	22			7.8	>100	0.0	275		

Table 1-24, con't.

Calendar Year 1983

Date	NO ₃ mg/l	Bac. MPN	Pesticides ¹ µg/l	NO ₃ in mg/l from other localities on Turkey River, and the Upper Iowa River at Decorah					
				Garber	Spillville	Above		Upper Iowa	
						Volga R.	Elkader		Elgin
1/4	39	All 16+							
1/11	34								
1/18	39								
1/25	32								
2/1	33								
2/8	31								
2/15	27								
2/22	9								
3/1	30								
3/2									
3/3	18		1.6A	21		17	19	19	
3/8	24								
3/15	32								
3/22	32								
3/29	32								
4/5	32								
4/7				32	36				31
4/12	30								
4/19	32								
4/26	32								
5/5	27			27		29	28	23	23
5/9	23								
5/10	29								
5/17	32								
5/19				34	40				41
5/24	24								
5/31	31								
6/7	28								
6/14	25								
6/17	28		0.51A	28			28	20	
6/21	26								
7/1	30								
7/2	34								
7/3	33								
7/5	47		0.93A						

Table 1-24, con't.

Date	NO ₃ mg/l	Bac. MPN	Pesticides ¹ µg/l	NO ₃ in mg/l from other localities on Turkey River, and the Upper Iowa River at Decorah					
				Garber	Spillville	Above		Upper Iowa	
						Volga R.	Elkader		Elgin
7/12	30								
7/19	24								
7/26	19								
8/2	23								
8/9	19			16	20				17
8/16	17								
8/23	17								
8/30	18								
9/6	15								
9/13	18								
9/20	15								
9/21				15	19				8
9/27	22								
10/4	18								
10/11	18								
10/18	23								
10/254	26								
11/1	24								
11/8	22								
11/15	24								
11/22	25								
11/29	31								
12/6	30								
12/13	30								
12/20	36								
12/27	30								

N-Series Analysis, mg/l
 4.5 NO₃-N
 0.57 Org-N
 0.01 Amm-N

Table 1-25. Water analyses for well JSW (site 83).

Date	NO ₃ mg/l	Bac. MPN	Radon pCi/l	pH	Turbid NTU	Temp. °C	Cond. micromhs/cm ² @ 25°C	Pesticides ¹ µg/l	Other ³ M	Notes
<u>1982</u>										
5/28	26	0						0.13A		
7/28	62	0								
8/25	28	0								
8/26	28	0								
11/30	32	0						N.D.		

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or 0
<u>1983</u>									
2/22	29	0							
5/5	31	0	7.2	11.8	720	7.00T 0.05G 0.01A	0.1A	14	M
6/28	30	0				6.50T 0.02G 0.04A			
7/3	27	0							
7/6	31	0				6.90T <0.01G <0.01A	0.11A		
7/28	28	0							
10/3	31			15	745		0.10A		

Table 1-26. Water analyses from St. Olaf (Galena) Spring (site 78).

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	Pesticides ¹ µg/l	N-Series ² mg/l	Cl ⁴ mg/l	Other ³ M or 0
<u>1982</u>									
1/26	42	16+							
6/23	44	16+							
8/25	33	16+							
11/30	54	16+							
11/30	56	16+							
12/29	68	16+							
<u>1983</u>									
3/3	40	16+							
5/4	62	16+							
7/6	91	16+							
7/28	53	16+							
8/31	38	16+							
10/3	39	16+		16	730				

Table 1-27. Water analyses for surfacewater sites RC-2 (site 115 on Robert's Creek) and SC-1 (site 114 on Silver Creek).

RC-2			SC-1		
Date	NO ₃ mg/l	Bac. MPN	Date	NO ₃ mg/l	Bac. MPN
8/25/82	23	All 16+	8/25/82	44	All 16+
11/30/82	42			17	
2/22/83	7			36	
3/3/83	27			48	
5/5/83	38	(Q=44 cfs)		49	
6/17/83	39		7/1/83	36	
7/28/83	38			40	
8/31/83	24			15	
10/3/83	22	(19°C; 680 sp. cond.)		35	(18°C; 820 sp. cond.)
12/13/83	42				

Table 1-28. Water analyses on tile-line discharge draining into sinkholes in Boogenhagen Basin; site BTL-D, downstream, draining fertilized pasture (in corn rotation).

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or 0
<u>1982</u>									
9/21	24						N.D.		
<u>1983</u>									
5/5	38			9.3	660				
6/17	66								
7/5	64						N.D.		
7/28	47								
7/29	47								
8/31	46								
10/3	38								
10/11									
10:30A	37								
3:30P	36								
8:30P	36								
10/12									
12:30A	36								
9:00A	37								
1:00P	38								
5:00P	37								
9:30P	37								
10/13									
7:45A	38								
4:30P	38								
10/14									
7:30A	38								
11/3	34			11	750				
12/12	37								

Table 1-29. Water analyses on tile-line discharge draining into sinkholes in Boogenhagen Basin; site BTL-U, upstream, draining corn field (BTL-1 of Hallberg et al., 1983).

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or O	
<u>1982</u>										
5/6	72	A11 16+					0.90A			
5/27	70						1.00A 6.50B 1.50L			
7/28	79						0.24A 0.08B			
9/21	69						N.D.			
12/28	84									
<u>1983</u>										
2/22	41									
3/3	70									
5/5	93		7.3	9.3	740	21.00T 0.52G 0.06A	N.D.	24	M	
6/17	96									
6/30	143						1.80A 0.40B			
	(130 from GT-1; tile draining adjacent corn field)									
	(123 from GS-1; interflow discharge in waterway above tiles --						0.86A) 0.29N)			
7/5	145						1.00A 0.11B			
	(138 from GT-1, as above)									
7/28	94									
7/29	94									
8/31	68									
10/3	69			17	790					
10/11										
10:30A	61									
3:30P	22									
8:30P	29									

Table 1-29. continued

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	Cl ⁴ mg/l	Other ³ M or O
10/12		A11 16+							
12:30A	34								
9:00A	55								
1:00P	57								
5:00P	59								
9:30P	60								
10/13									
7:45A	63								
4:30P	67								
10/14									
7:30A	67								
11/3	74								
12/12	72								
						16.00T 0.05NO2 <0.01G <0.01A			

Table 1-30. Water analyses on surfacewater draining to sinkholes in Boogenhagen Basin; site Boog-D, downstream (BSW-1 of Hallberg et al., 1983).

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or 0
<u>1982</u>									
5/6	27	A11 16+					6.30A 31.00B 12.70L 1.50S		
5/27	14 (35, at sinkhole, BSW-3)								
<u>1983</u>									
2/22	14								
3/3	35								
5/5	47	*Q=1.3 cfs (suspended sediment concentration - 135 mg/l)	16.5	640			0.10A		
5/13	45	Q=2.3 (sus. sed. con. - 34 mg/l)				10.0T		25	
						1.7G 0.74A			
5/18 7:20A	34	Q=3.0 (sus. sed. con. - 415 mg/l) (Pesticide in sediment 1.1A 3.5 R 0.6-Dieldrin)				7.6 1.7G 0.08A	1.0A 0.42B 0.42L		
10:00P		Q=2.3 (sus. sed. con. - 200 mg/l)							
6/27 8:00P	49	Q=0.9 (sus. sed. con. - 150 mg/l)	7.3	720		11.0T 2.8G 1.9A	2.8A 0.2B 0.18L	30	M
6/28 3:20P	57	Q=1.0 (sus. sed. con. - 36 mg/l)					1.60D		
6/29 7:40P	8	Q=25-30 (sus. sed. con. - 6,324 mg/l)	7.0	180		14.T 35.0G 2.5A		8.0	M
9:10P	12								
6/30 7:00A	68	Q=3.4 (sus. sed. con. - 70 mg/l)				15.0T 0.95G 0.10A	3.8A 0.27B 0.18L		

Table 1-30. Continued.

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or 0
7/1	11	Q=8							
7/5	69	Q=4.5 (sus. sed. con. - 10 mg/l)	7.6		720		0.69A 0.12B	20	M
7/8	69	Q=2.6 (sus. sed. con. - 10 mg/l)	7.6		700		0.53A	20	M
7/28	58	Q=0.3							
8/31	42								
10/3	32			18	835				
10/11									
	10:30A	29							
	3:30P	<5							
	8:30P	<5							
10/12									
	12:30A	22							
	9:00A	41							
	1:00P	44							
	5:00P	44							
	9:30P	46							
10/13									
	7:45A	45							
	4:30P	48							
10/14									
	7:30A	51							
11/3									
		48							
12/13									
		55							

*Q = stream discharge

Table 1-31. Water analyses on surfacewater draining to sinkholes in Boogenhagen Basin; site Boog-U, upstream (BSW-2 of Hallberg et al., 1983).

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or O
<u>1982</u>									
5/6	51	A11 16+					1.40A 8.00B 4.00L 3.30S		
5/27 7/23	43 25						0.13A		
<u>1983</u>									
5/4	77								
5/5	60	Q=0.6 cfs (Suspended Sediment Concentration - 460 mg/l)	8.3	12	660	14.0T 0.58G 0.03A	0.10A	20	M
5/13	54	Q=0.6 (sus. sed. con. - 30 mg/l)				12.0T 1.2G 0.30A			
5/18 7:20A	49	Q=2.0 (sus. sed. con. - 70 mg/l)				11.0T 0.90G 0.07A	0.44A 0.21B 0.37L		
10:00A	46		7.5		620	10.0T 1.5G 0.69A	0.69A 0.26B 0.31L	18	M
5/19 9:30A	55	Q=1.1 (sus. sed. con. - 38 mg/l)	7.5		620	12.0T 1.1G 0.14A	2.1A 0.55B 0.56L	21	M
6/27 8:50P	42	Q=0.5 (sus. sed. con. - 39 mg/l)	7.4		700	9.4T 2.5G 1.9A	2.8A 0.10B 0.10L 0.20D	16	M
6/28 3:00P	70	Q=0.3 (sus. sed. con. - 17 mg/l)							

Table 1-31. Continued.

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or O
6/29 7:00P	11 (sus. sed. con. - 5807 mg/l)						6.6A 5.0B		
6/30 7:00A	76		7.6		620		3.8A 0.27B 0.18L	18	M
7/5	86	Q=1.3	7.6		700	19.0T 0.31G 0.05A	0.71A 0.13B	23	M
7/8	83	Q=0.4	7.4	22	700	19.0T 0.31G 0.04A	0.71A 0.13B	23	M
7/28	70	Q=0.03							
8/31	62								
10/3	47			16	845				
10/11 10:30A 3:30P 8:30P	<5 <5 <5								
10/12 12:30A 9:00A 1:00P 5:00P 9:30P	38 50 53 53 54								
10/13 7:45A 4:30P	56 58								
10/14 7:30A	61								
12/13	66								

Table 1-32. Water analyses from tile-line discharge stream draining into sinkhole in Sass basin; site ES-E (east-side)

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or O
1982	Tile drains hayfield (alfalfa) and corn.								
5/6	51	A11 16+							
5/27	60								
1983	PIK acreage								
6/29	73								
1984									
3/8	67								
4/30									
1415	42								
1930	47								
5/1									
0030	50								
1030	51								
1740	53								
5/4	57	(Planted to alfalfa meadow, cut for hay.)							
5/8	61								
5/17	71								

Table 1-33. Water analyses from tile-line discharge stream draining into sinkhole in Sass basin; site ES-W (west-side)

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or O
1982	Tile drains cornfield								
5/6	88	A11 16+							
5/27	96								
1983	Corn								
6/29	78								
2030									
1984									
3/8	66								
5/1									
0030	66								
1030	68								
1750	67								
5/4	73	(Planted to corn.)							
5/8	69								
5/17	79								

Table 1-34. Water analyses on surfacewater draining to sinkholes in Sass basin; drains cornfields, pasture, and alfalfa hayfield.

Date	NO ₃ mg/l	Bac. MPN	pH	Temp. °C	Cond.	N-Series ² mg/l	Pesticides ¹ µg/l	C1 ⁴ mg/l	Other ³ M or O
1982									
5/6	30	All 16+					1.90A 7.20B 3.30L		
5/27	43								
1983									
6/29 8:30P	13	(During runoff.)							
6/29	<5	(surfacewater runoff draining into sinkhole.)							
1984									
4/30 2:30P	49								

APPENDIX 2

Water Mineral-Scan Analyses From Various Monitoring Sites

Table 2-1. Major ion analyses from network sites, 5/5/1983

Site	Well Number	K	Na	Ca	Mg	Mn	NO ₃	F	Cl	SO ₄	HCO ₃	Total Fe
11	(VD-24)	1.0	8.8	91	37	0.02	21	0.2	14	52	372	0.03
16	(VD-12)	1.1	12	81	33	0.08	23	0.2	9.0	42	344	7.3
26	(B-32)	0.8	6.4	100	45	0.06	64	0.3	9.0	84	426	7.4
30	(B-27)	ND	5.6	84	40	0.02	29	0.1	3.0	15	407	3.9
37	(VD-18)	0.9	14	120	41	0.04	62	0.3	34	56	383	2.2
39	(L-7)	1.3	20	140	57	ND	140	0.2	80	53	376	0.12
45	(PAT-20)	2.0	8.9	98	31	0.03	0.7	0.3	ND	7.5	440	0.88
47	(PAT-18)	1.3	6.2	84	30	0.15	ND	0.25	ND	12	384	6.5
49	(F-51)	1.7	5.6	89	32	0.57	11	0.4	14	42	342	3.4
56	(F-33)	0.2	10	100	38	ND	38	0.2	11	46	372	0.06
57	(T-17)	ND	10	91	40	ND	65	0.2	28	27	342	0.05
75	(GL-8)	ND	260?	1.1?	0.4?	0.08	94	0.25	46	60	417	0.08
81	(AB-6)	0.9	3.6	62	20	ND	36	0.2	4.0	19	229	0.11
82	(BS)	2.5	11	89	39	0.02	45	0.2	16	26	364	0.07
83	(JSP)	2.7	12	94	39	ND	31	0.1	14	31	384	0.03
84	(AB-3)	3.3	22	100	47	0.27	37	0.4	44	56	400	3.1
108	(L-22)	ND	8.0	74	30	0.02	66	0.2	20	28	237	0.02
111	(F-47)	2.8	14	81	33	0.22	40	0.4	22	21	308	0.28
--	(BTL-1)	1.5	13	86	39	ND	93	0.1	24	26	296	ND

Table 2-1. Continued.

Site	Soluble Fe	SiO ₂	Conductivity	TDS	Hardness	Alkalinity	pH
11	0.03	16	730	409	380	305	7.3
16	7.3	21	700	413	351	282	7.4
26	7.4	20	840	483	453	349	7.25
30	3.9	23	700	381	381	334	7.3
37	2.2	21	900	482	462	314	7.3
39	0.12	18	1200	653	577	308	7.2
45	0.88	16	680	335	374	361	7.3
47	6.5	19	600	323	345	315	7.4
49	3.4	21	640	385	361	280	7.4
56	0.06	19	700	407	369	274	7.45
57	0.05	18	750	428	406	305	7.3
75	0.08	21	860	491	428	321	7.2
81	0.11	15	480	293	237	188	7.5
82	0.07	17	730	379	383	298	7.2
83	0.03	16	720	401	395	315	7.3
84	3.1	19	900	626	456	328	7.85
108	0.02	17	620	296	308	194	7.05
111	0.28	2.0	660	340	339	263	8.4
--	ND	14	740	392	375	243	7.25

KEY: K = Pottasium
 Na = Sodium
 Ca = Calcium
 Mg = Magnesium
 Mn = Manganese - soluble Mn
 NO₃ = Nitrate
 F = Flouride
 Cl = Chloride
 SO₄ = Sulfate
 HCO₃ = Bicarbonate
 Fe = Iron
 SiO₂ = Silica
 Conductivity = Specific conductance
 TDS = Filterable Residue
 Time = Military style; i.e., 3:30 pm = 1530
 ND - not detected - use for < (less thans)

Table 2-2. Major ion analyses from Big Spring.

Date	Time	K	Na	Ca	Mg	Mn	NO ₃	F	Cl	SO ₄	HCO ₃	Total Fe
<u>1983</u>												
5/5	---	2.5	11	89	39	0.02	45	0.2	16	26	364	0.07
5/18	---	1.9	7.6	84	36	ND	44	0.1	17	28	362	ND
5/19	---	2.1	7.8	83	36	0.03	46	0.1	16	26	359	0.16
6/27	2200	0.8	10	88	39	0.03	44	0.1	19	26	367	0.43
6/28	1125	1.4	11	89	36	0.05	40	0.1	16	24	368	0.35
	1730	2.1	9.6	89	36	0.04	44	0.1	19	22	359	0.54
6/30	1040	4.1	9.7	86	34	ND	44	0.1	18	20	343	0.77
	1600	4.2	9.4	84	36	0.03	45	0.1	18	20	332	0.85
	2220	4.5	7.1	83	33	0.02	47	0.1	17	21	331	0.51
7/1	600	3.6	8.0	77	30	0.03	45	0.1	14	18	307	1.6
	1350	3.4	8.7	80	34	0.06	53	0.1	16	19	309	3.8
	2220	5.3	6.7	63	21	0.19	44	0.1	12	15	238	5.9
7/5	1630	1.4	6.5	86	35	ND	55	0.15	16	22	347	0.40
7/8	1100	0.8	6.7	91	37	ND	55	0.2	17	24	359	0.17
7/29	---	0.6	7.0	90	28	0.01	42.5	0.2	18	25	373	0.10

Table 2-2. Continued.

Date	Soluble Fe	SiO ₂	Lab Conductivity	TDS	Total Solids	Hardness	Alkalinity	pH
<u>1983</u>								
5/5	0.07	17	730	379	379	383	298	7.2
5/18	ND	16	720	431	431	358	297	7.35
5/19	0.16	20	720	427	427	356	294	7.3
6/27	0.43	18	720	488	488	381	301	7.3
6/28	0.35	18	710	486	486	371	302	7.4
	0.54	18	710	464	464	384	294	7.2
6/30	0.07	16	700	424	499	356	281	7.4
	0.06	16	690	411	474	360	271	7.2
	0.08	16	830?	403	511	344	271	7.4
7/1	0.11	16	640	389	690	310	252	7.4
	0.15	17	650	408	1952	349	253	7.3
	0.25	16	520	339	1706	257	195	7.2
7/5	0.03	18	710	455	460	360	285	7.25
7/8	ND	18	730	443	454	380	294	7.3
7/29	0.10	17	760	415	415	381	306	7.2

KEY: K = Potassium
 Na = Sodium
 Ca = Calcium
 Mg = Magnesium
 Mn = Manganese - soluble Mn
 NO₃ = Nitrate
 F = Flouride
 Cl = Chloride
 SO₄ = Sulfate
 HCO₃ = Bicarbonate
 Fe = Iron
 SiO₂ = Silica
 Conductivity = Specific conductance
 TDS = Filterable Residue
 Time = Military style; i.e., 3:30 pm = 1530
 ND - not detected - use for < (less thans)

Table 2-3. Major ion analyses from sites Boog-U and Boog-D.

Date	Time	K	Na	Ca	Mg	Mn	NO ₃	F	Cl	SO ₄	HCO ₃	Soluble Fe
1983												
BOOG-U												
5/5	---	2.5	12	76	35	0.08	60	0.1	20	23	310	0.11
5/18	1000	8.5	8.3	67	31	0.30	46	0.1	18	24	287	1.0
5/19	0930	4.9	9.1	67	30	0.25	55	0.1	21	20	276	0.61
6/27	2050	15	11	73	32	0.92	42	0.1	16	22	322	0.61
6/29	1900	11	2.5	18	5.8	1.2	6.2	0.1	8.0	13	85	0.68
7/05	---	2.2	8.1	73	32	0.03	82	0.1	22	19	268	0.05
7/08	---	1.6	8.4	79	34	0.05	83	0.1	23	17	290	0.03
BOOG-D												
6/27	2000	17	13	75	35	0.55	49	0.1	30	24	318	0.23
6/30	0700	4.8	8.8	69	29	0.13	69	0.1	18	17	254	0.20
7/05	---	2.3	7.3	76	34	0.11	69	0.1	20	21	290	0.04
7/08	---	1.4	7.7	78	36	0.1	72	0.15	20	21	309	0.03

Table 2-3. Continued.

Date	Total Fe	SiO ₂	Conductivity	TDS	Total Solids	Hardness	Alkalinity	pH
1983								
BOOG-U								
5/5	0.21	7.6	700	390	390	334	255	8.3
5/18	1.0	17	620	451	451	297	235	7.5
5/19	0.61	16	620	420	420	292	226	7.5
6/27	0.85	19	700	431	614	316	264	7.4
6/29	7.5	7.9	180	230	1460	85	70	7.0
7/05	0.11	15	680	271	406	314	219	7.55
7/08	0.25	15	700	405	426	338	237	7.4
BOOG-D								
6/27	0.36	18	720	489	575	333	261	7.3
6/30	0.49	16	620	358	476	293	208	7.6
7/05	0.68	16	720	398	438	331	238	7.6
7/08	0.36	16	700	428	482	344	254	7.6

KEY: K = Potassium
 Na = Sodium
 Ca = Calcium
 Mg = Magnesium
 Mn = Manganese - soluble Mn
 NO₃ = Nitrate
 F = Flouride
 Cl = Chloride
 SO₄ = Sulfate
 HCO₃ = Bicarbonate
 Fe = Iron
 SiO₂ = Silica
 Conductivity = Specific conductance
 TDS = Filterable Residue
 Time = Military style; i.e., 3:30 pm = 1530
 ND - not detected - use for < (less thans)

APPENDIX 3

Chemical Analyses From Soil Profile Samples From The Big Spring Basin

*Pesticide abbreviations as in Appendix 1: A - Atrazine; B - Bladex; D- Dual;
F - Dyfonate; L - Lasso; R - Furadan; S - Sencor/Lexone; N - dieldrin; ND -
none detected; N/A or blank - not analyzed.

Depth inches (cm)	Soil Horizon or Weathering Zone	Nitrate mg/kg	Pesticides* µg/kg	Total Phosphorus %	Radium; ²²⁶ Ra pCi/g	Materials
Site 22HB-1; Downs soil in Wisconsinan loess, on upland interfluvial summit; in 2nd year of corn after meadow (11/13/82).						
0-7 (0-18)	Ap	40.0	110.0A 23.0L 5.0F	0.04	2.2	Loess
29-35 (74-89)	B2t	17.0	12.0A	0.05		
88-95 (224-241)	C-MOU	9.0	ND	0.07		
116-120 (295-305)	C-DU	7.6	N/A			
148-162 (376-411)	DU/DL	6.7	N/A			

Site 22HB-7; Tama soil in Wisconsinan loess, on upland divide; in continuous corn (11/4/82).

0-7 (0-18)	Ap	31.0	80.0A 2.0L 8.5F	0.04	1.9	Loess
16-20 (41-50)	A3	38.0	1.0A	0.03	N/A	
36-48 (91-122)	Bt	43.0	1.0A	0.05	2.0	
80-88 (203-224)	C-MOU	32.0	ND	0.07	N/A	
102-110 (260-279)	C-MDU	18.0	0.3A			
136-140 (345-356)	DU	11.7				

Depth inches (cm)	Soil Horizon or Weathering Zone	Nitrate mg/kg	Pesticides* µg/kg	Total Phosphorus %	Radium; ²²⁶ Ra pCi/g	Materials
Site 22HB-10; In Arenzville soil mapping unit; Late Holocene alluvium along Robert's Creek, in continuous corn (11/3/82), near F-45.						
0-6 (0-15)	Ap	74.0	120.0A 17.0L 10.0F 2.0N	0.06	N/A	Silt loam, Camp Creek Member (post-settlement alluvium)
15-20 (38-50)	Alb	37.0	1.4A	0.05	1.4	Silt loam, Late Holocene alluvium
35-40 (89-101)	A3b	59.0	1.0A			As above
80-84 (203-213)	C(RL)	10.0	1.0A			Stratified loam and sand
100-104 (254-264)	C(MOL-MOU)	0.3*				Sand and gravel

* Below water table.

Site 22HB-11; In Huntzville soil mapping unit; Mid-Holocene alluvium along Robert's Creek; in continuous corn (11/3/82).

0-7 (0-18)	Ap	55.0	3.6A 5.8B 9.1L 15.0N			Silt loam, Camp Creek Member (post-settlement alluvium)
39-48 (99-122)	Alb	70.0	1.8A 1.8N			silt loam, mid-Holocene alluvium
70-75 (178-191)	Bltb	36.0	1.1A 0.8N			as above

Depth inches (cm)	Soil Horizon or Weather- ing Zone	Nitrate mg/kg	Pesticides* µg/kg	Total Phosphorus %	Radium; 226Ra pCi/g	Materials
Site 22 AB-22; in Arenzville soil mapping unit, on Mid-Holocene terrace and alluvium; in long-term, fertilized pasture (6/17/83).						
0-6 (0-15)	A/C	19.0				Silt loam - Post-settle- ment alluvium
6-12 (15-30)	A1	16.0				Silt loam - mid-Holocene alluvium
12-18 (30-46)	A2	8.0				
18-24 (46-61)	B/A	6.0				
24-36 (61-91)	B/A	6.4				
36-44 (91-112)	B1	12.0				
48-68 (122-172)	B3	6.9				
68-85 (172-216)	C-MRL	6.4				
85-103 (216-262)	MRL	2.5				
Site 22-43-FL; in small feedlot on gentle side-slope over loess-derived soil (10/13/83).						
0-4 (0-10)	"0"	62.0				manure and silt loam
10-14 (25-36)	O/A	75.0				silt loam with manure
18-24 (46-61)	Btg	7.8				silt loam-loess
34-38 (86-97)	Btg	6.6				
46-50 (117-127)	C-MDL	2.5				
54-60 (137-152)	C-OL	2.1				

Depth inches (cm)	Soil Horizon or Weather- ing Zone	Nitrate mg/kg	Pesticides* µg/kg	Total Phosphorus %	Radium; 226Ra pCi/g	Materials
Site 22 AB-20; in Fayette soil in Wisconsinan loess; on interfluvial summit; in oak, hickory, walnut woodlot at least 50 years old (6/17/83).						
0-6 (0-15)	A1-E	34.0	ND			Loess
6-12 (15-30)	E2	3.5	ND			
13-18 (30-45)	E/Bt	3.7				
18-24 (46-64)	B2t	5.1	ND			
24-30 (64-76)	B3t	4.5	ND			
30-42 (76-107)	B4-B6t	4.0				
54-60 (139-150)	B9t	2.6				
79-100 (254-305)	C-MDL	4.3				
100-120 (254-305)	DL	2.7				
126-132 (320-335)	CR	2.6				Bedrock-dolo- mitic silt- stone; Elgin Member, Maquo- keta Frm.
Site 22 RB-1; in Dubuque soil in Wisconsinan loess over bedrock, on sideslope of interfluvial; in mixed woodlot, at least 40 years old (6/17/83).						
0-8 (0-20)	A1	36.0				Loess
8-14 (20-36)	E1	8.9				
14-19 (36-48)	E/BW	6.2				
19-24 (48-61)	BCr	2.8				Bedrock-dolo- mitic silt- stone; Elgin Member, Maquo- keta Frm.

Depth inches (cm)	Soil Horizon or Weathering Zone	Nitrate mg/kg	Pesticides* ug/kg	Total Phosphorus %	Radium; ²²⁶ Ra pCi/g	Materials
-------------------	---------------------------------	---------------	-------------------	--------------------	---------------------------------	-----------

Site 22 BSN-1; in eroded Fayette soil, in Wisconsin loess on shoulder of interfluvium; first year in corn, timber cleared fall of 1982 (10/14/83)

0-6 (0-15)	Ap	18.0	100.0A 15.0L			Loess
6-12 (15-30)	Bt	44.0	18.0A 2.4L			
12-18 (30-46)	Bt	17.0				
18-24 (46-61)	Bt	6.7				
24-36 (61-91)	Bt	6.1				
36-48 (91-122)	C-MOL	2.6				
48-60 (122-152)	C-MOL	2.9				

Site 22 AB4U; in eroded Fayette soil, in Wisconsin loess, on upland summit; in second year of alfalfa-timothy-clover hay field rotation; low chemical-N rotation (10/13/83).

0-6 (0-15)	Ap	4.0				Loess
6-15 (15-30)	B1t	2.1				
24-30 (61-75)	B3t	2.2				
36-40 (91-101)	B5t	2.6				
80-84 (203-213)	C-MOU	8.6				
120-128 (305-325)	OU	4.1				
132-136 (335-345)	2Ab	8.9				Basal loess sediments and Paleosol

226

Depth inches (cm)	Soil Horizon or Weathering Zone	Nitrate mg/kg	Pesticides* ug/kg	Total Phosphorus %	Radium; ²²⁶ Ra pCi/g	Materials
-------------------	---------------------------------	---------------	-------------------	--------------------	---------------------------------	-----------

Site 22 AB-41; in Fayette soil in Wisconsin loess, on summit of high terrace along Robert's Creek; in pasture with scattered timber (10/14/83).

0-6 (0-15)	A	6.5	0.6N			Loess
12-18 (30-46)	E/B	5.9	ND			
24-30 (61-76)	B3t	4.8	ND			
36-40 (91-101)	B4t	7.8				
46-52 (117-132)	B6t	5.9				
54-60 (137-152)	Bt/C	11.0				
68-74 (172-188)	C-MOL	10.0				
104-110 (264-279)	OU	7.2				
120-128 (305-325)	OU	5.1				
146-156 (371-396)	OU	4.6				Interbedded silts and fine sands
172-176 (437-447)	OU	3.3				Interbedded fluvial silts and sands
185-188 (470-478)	OU	5.6				

227

Depth inches (cm)	Soil Horizon or Weather- ing Zone	Nitrate mg/kg	Pesticides* µg/kg	Total Phosphorus %	Radium; 226Ra pCi/g	Materials
Site 22 AB-42; in Tama soil (with grainy coats), in Wisconsinan loess, on summit of high loess-mantled terrace/bench above Robert's Creek (10/13/83).						
0-6 (0-15)	Ap	14.0	30.0A 5.8B 7.7L 2.1F 2.0N			Loess
8-12 (20-30)	A1	22.0				
12-18 (30-46)	A1	32.0				
22-24 (56-61)	Bt/A	28.0				
58-62 (147-157)	Bt/C	19.0	2.1A 0.5N			
80-84 (203-213)	C/Bt	9.0				
110-120 (279-305)	C-01	22.0				
140-150 (356-381)	C-MOL	17.0				
170-177 (432-450)	OU-MOU	14.0	0.3A			Interbedded silt loam and fine sandy loam
187-191 (475-485)	OU	22.0				Alluvial lag, loam with gravel
200-210 (508-533)	OU	8.0				Sand and gravel above bedrock

Depth inches (cm)	Soil Horizon or Weather- ing Zone	Nitrate mg/kg	Pesticides* µg/kg	Total Phosphorus %	Radium; 226Ra pCi/g	Materials
Site 22 AB-43; in Fayette soil, in Wisconsinan loess, on summit of upland interfluvium; in continuous corn (10/13/83).						
0-6 (0-15)	Ap	4.6	11.0A 0.6N			Loess
6-12 (15-30)	E/B	6.1	6.0A 2.1L			
12-18 (30-46)	Bt	4.0				
18-24 (46-61)	Bt	8.0				
24-33 (61-84)	Bt	14.0				
33-39 (84-100)	Bt	7.6	6.0A			
46-52 (117-132)	C/B	18.0	2.6A			
59-62 (150-157)	C-MOL MOL	7.2	ND			
64-68 (162-172)	MOU-MDU	10.0				
72-76 (182-193)	MOU	16.0	1.1A			
92-98 (234-250)	MOU	36.0				
116-120 (295-305)	OU	27.0				
130-136 (330-345)	MOJL	15.0				Till

Depth inches (cm)	Soil Horizon or Weather- ing Zone	Nitrate mg/kg	Pesticides* µg/kg	Total Phosphorus %	Radium; 226Ra pCi/g	Materials
Site F-45 US; in Arenzville soil mapping unit; in silty Mid-Holocene alluvium along Robert's Creek; in continuous corn (11/2/83).						
0-8 (0-20)	Ap	36.0				silt loam; late Holocene alluvium.
21-25 (53-64)	AB	7.8				silt loam; late Holocene alluvium.
89-95 (226-241)	C-MOL	1.2				silt loam; late Holocene alluvium.

Site 22 AB-45; in Arenzville soil mapping unit; silty Camp Creek Member (post-settlement deposits) over buried soil developed in silt loam and heavy silt loam late Holocene alluvium along Deer Creek; 2nd year corn; never chemical-N fertilizer used (11/3/83).

0-8 (0-20)	Ap	31.0				silt loam, Camp Creek member
24-30 (61-76)	C-OL	22.0				silt loam, Camp Creek member
48-55 (122-140)	Ab	13.0				silt loam, Camp Creek member

Site 22 AB-46; in Festina soil mapping unit; Early Holocene terrace along Deer Creek; silty alluvium; second year corn; former farmstead; never chemical-N fertilizer used (11/3/83).

0-6 (0-15)	AB	33.0				silt loam; early Holocene alluvium
20-26 (50-66)	B2	12.0				silt loam; early Holocene alluvium
34-40 (86-101)	B3t					silt loam; early Holocene alluvium
48-55 (122-152)	C-MOL	7.6				

Depth inches (cm)	Soil Horizon or Weather- ing Zone	Nitrate mg/kg	Pesticides* µg/kg	Total Phosphorus %	Radium; 226Ra pCi/g	Materials
Site 22 AB47; in Dubuque soil mapping unit; thin Wisconsinan loess/colluvium, over bedrock; 2nd year corn; low level of N fertilization (11/2/83).						
0-7 (0-18)	Ap	25.0				Loess/colluvium
7-14 (18-36)	R/Bt	10.0				Dolomitic silt- stone; Elgin Member, Maquo- keta Frm.
16-26 (41-66)	B/C/R	13.0				
Site 22-5R; in Dubuque soil mapping unit; thin loess colluvium over bedrock; continuous corn (10/24/83).						
0-8 (0-20)	Ap	34				Loess/colluvium
8-18 (20-46)	Bt	22				
18-24 (46-61)	B	17				
24-32 (61-81)	B/C/R	32				Loess/colluvium and Galena dolomite

* A - atrazine; B - Bladex; L - Lasso; F - Dyfonate; N - Dieldrin
ND - none detected; N/A (or blank) - not analyzed.